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Statistical properties of momentum transfer in two-phase flow*

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Abstract—The momentum transfer in a two-phase stream, consisting of particles carried by a fluid, was studied by applying the statistical theory of turbulence. Statistical relations showed that the correlation, scale and intensity of one phase can be calculated from those of the other phase. Approximate solution indicates the basic parameters affecting momentum transfer.

Résumé—En appliquant la théorie statistique de la turbulence, l'auteur étudie le transfert des quantités de mouvement dans un courant à deux phases constitué de particules transportées par un fluide.

Des relations statistiques montrent que les caractéristiques, proportion et intensité d'une phase, peuvent se calculer à partir des caractéristiques de l'autre phase.

A l'aide de solutions approchées, l'auteur trouve les paramètres de base, affectant le transfert de la quantité de mouvement.

INTRODUCTION

THE characteristics of momentum transfer in a two-phase stream consisting of liquid or solid particles in a gas, or solid particles in a liquid, is of fundamental interest in the following fields of study and techniques of measurement:

1. In using solid particles as tracers in studying flow of fluids, the proximity of the particle motion to stream motion should be known [1].**

2. In a fluidized bed of catalyst, the diffusivity of the continuous phase can be measured with relative ease, but the diffusivity of the particles has not been taken care of [2].

3. In the combustion of solid fuel particles or liquid fuel droplets, the diffusion between the fuel and air is influenced by the relative motion of the fuel particles and the air stream [3].

4. In sedimentation studies and pneumatic

conveying, efforts have been made toward finding the relation between the motion of solid particles and the fluid stream [4, 5].

The purpose of this paper is to present the relations between the intensities and scales of the two phases arrived at from the statistical theory of turbulence, together with an approximate solution which indicates the basic parameters affecting the momentum transfer between the two phases.

The two phase fluid under consideration will be a fluid stream carrying spherical solid particles of uniform size. In this system, mass transfer is absent and heat transfer is negligible between the two phases. The following assumptions have been made in the following analysis:

1. The turbulence of the fluid stream is isotropic and non-decaying.

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** Numbers in brackets refer to references at the end of the paper.

2. The relative velocity between the solid particles and the stream gives, at all times, a Reynolds number of the particles of order 1 or less.
3. The particles are relatively far apart so that the inter-action between the particles can be neglected (see Appendix I).
4. The average velocity of the solid particles is equal to that of the fluid stream and is a constant.*

The case of pendulum motion of a particle in a turbulent stream was studied by C. C. LIN [6]. However, application of the Eulerian correlation in the present case would require the inclusion of the probability of the existence of a particle at a given location [4]; Lagrangian correlation is introduced here so that the velocity of a single particle is described along its journey. In the Lagrangian case, the rapidity of fluctuation of velocity in time or its character is not altered by the presence of the average velocity of the main stream. Therefore, the Lagrangian statistical frequency function $f_\eta(\eta)$ is fundamentally different from that of the Eulerian, $f(\eta)$ [7]; the difference is pointed out in the following.

In adopting the Lagrangian correlation, the velocity of a fluid particle becomes related to the time co-ordinate or its velocity following its motion, and the velocity of a fluid particle at a fixed point becomes insignificant (although the relation between the space location and the time coordinates can be taken care of through the integral of velocity components with respect to time). Following the fourth assumption in the above, the velocity of the solid particle and the velocity of the stream are related to the same time co-ordinate, although not the same space co-ordinate. In other words, for the case under consideration, the velocity of a single solid particle and the velocity of fluid motion are related to the same time coordinate, and we are concerned only with the velocity of the fluid stream in the neighbourhood of a solid particle.

* The problem of acceleration of the particles from rest by a fluid stream of uniform velocity was sufficiently treated in reference [5].

FUNDAMENTAL RELATIONS

Here the concept of spectrum of turbulence [7] is made use of. Due to isotropy of turbulence of the stream, which flows horizontally with a constant average velocity U , the axial component, u , (relative to U) of turbulence of the stream will be representative of all three components. In terms of the velocity spectrum

$$u = \sum_n A_n \sin 2\pi n t = v, \quad (1)$$

where A_n is the amplitude of the n^{th} harmonic and n is the frequency. The intensity of turbulence :

$$\bar{u}^2 = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T u^2 dt = \frac{1}{2} \sum A_n^2 = \bar{u}^2 \int_0^\infty f_\eta(\eta) d\eta, \quad (2)$$

where $f_\eta(n)$ is the Lagrangian statistical frequency function, and

$$\int_0^\infty f_\eta(n) d\eta = 1. \quad (3)$$

Extending TAYLOR's hypothesis to the Lagrangian system :

$$R_\eta = \frac{\overline{u(t)u(t-\xi)}}{\bar{u}^2} = \frac{\sum A_n^2 \cos 2\pi \eta \xi}{\sum A_n^2}, \quad (4)$$

which is a time correlation rather than that of equating Eulerian space correlation to Eulerian time correlation in the Eulerian system of turbulence spectrum.

By the definition of $f_\eta(n)$, R_η can be expressed in terms of a Fourier integral :

$$R_\eta = \int_0^\infty f_\eta(n) \cos 2\pi n \xi dn = \int_0^\infty f_\eta(n) \cos 2\pi \frac{n\eta}{\sqrt{u^2}} dn, \quad (5)$$

where $d\eta = \sqrt{u^2} dt$, and for non-decaying turbulence, $\eta = \sqrt{u^2} t$. Hence, as analogous to the Eulerian cases, R_η and $f_\eta(n)$ are Fourier transforms [8].

The above relation implies that the velocity of a single particle of the stream is described along its journey, and the rapidity of its fluctuation in time is not altered by the average velocity U of

the main stream. The concept of diffusion by continuous movement gives [9]:

$$\frac{1}{2} \frac{d}{dt} (\overline{X^2}) = \overline{u^2} \int_0^t R_\xi d\xi$$

or

$$\frac{1}{2} \frac{d}{dt} (\overline{X^2}) = \int_0^{\eta_2} R_\eta d\eta,$$

where $\overline{X^2}$ is the average displacement.

Further, the scale of turbulence of the stream is given by:

$$l_1 = \int_0^T R_\eta d\eta, \quad (6)$$

and the A_η defined by the parabola in Fig. 1 is given as:

$$\frac{1}{A_\eta^2} = \lim_{\eta \rightarrow 0} \left(\frac{1 - R_\eta}{\eta^2} \right) \quad (7)$$

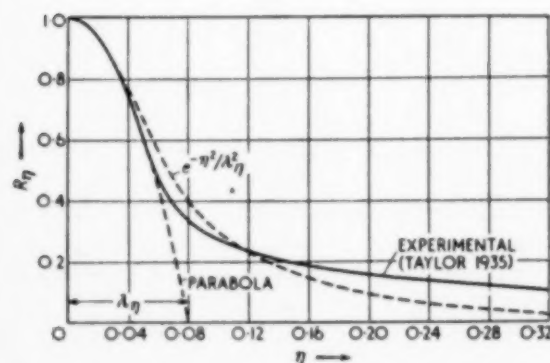


FIG. 1. Approximations to Lagrangian correlation curve.

The case of motion of a spherical pendulum in a viscous fluid was treated by STOKES as presented in Reference [10]. Since in this present study we are interested in small solid particles having very small motion relative to the stream (in terms of relative frequency between the particle and the stream), the correction for increase in apparent inertia and the diminution of oscillation [10] can be neglected. Therefore, neglecting the squares and products of the relative velocity between the fluid and the solid particle, and for

constant average velocity of the main stream,* the motion of the particles can be described by (for small relative motion defined by assumption (2) in the above):

$$\frac{d u_p}{dt} = F(u - u_p), \quad (8)$$

where

$$F = \frac{18 \mu}{d_p^2 \rho_p} [12]$$

F has the dimension of $(\text{time})^{-1}$ and is characteristic of the time response of the particle. Equation (8) was obtained through simplification by the comparison of order of magnitudes rather than simply an engineering postulate. Solving Equation (8) with u given in Equation (1):

$$\begin{aligned} u_p &= F \sum_n \frac{2\pi n A_n}{F^2 + (2\pi n)^2} \left[\frac{F}{2\pi n} \sin 2\pi n t - \cos 2\pi n t \right] \\ &= \sum_n \frac{A_n}{\sqrt{1 + \left(\frac{2\pi n}{F}\right)^2}} \sin(2\pi n t - \theta_n), \end{aligned} \quad (9)$$

where θ_n is the phase lag and $\theta_n = \tan^{-1} \left(\frac{2\pi n}{F} \right)$. To calculate the vertical component of the turbulent velocity of the particle, neglecting the gravity effect on the stream but considering the gravity effect on the particle:

$$\frac{dv_p}{dt} = F(v - v_p) + g, \quad (10)$$

where g is the acceleration due to gravity, which gives:

$$\begin{aligned} v_p &= F \sum_n \frac{2\pi n A_n}{F^2 + (2\pi n)^2} \\ &\quad \left[\frac{F}{2\pi n} \sin 2\pi n t - \cos 2\pi n t \right] + \frac{g}{F} \end{aligned} \quad (11)$$

The intensity of turbulence of the particles are respectively:

$$\overline{u_p^2} = \frac{1}{2} \sum_n \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2}, \quad (12)$$

* The case of an accelerated field without turbulence was treated recently by GILBERT and others [11].

and

$$\overline{u_p^2} = \frac{1}{2} \sum_n \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2} + \frac{g^2}{F^2}. \quad (13)$$

Therefore, in general, where gravity effect is considerable, the turbulent motion of the particles is anisotropic. For excessively large particles such that the terminal velocity is much greater than $\overline{u^2}$, $\overline{v_p^2}$ has no meaning, nor $\overline{u_p^2}$, as the particle would fall quickly to the bottom of the duct. (See Appendix for carrying capacity of a turbulent stream.) For cases of small particles and therefore large F , isotropy of the turbulent motion of the particles can be assumed. Hence

$$\overline{u_p^2} = \frac{1}{2} \sum_n \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2} \approx \overline{v_p^2}. \quad (14)$$

By the definition of the frequency function (Equation 2):

$$\frac{1}{2} A_n^2 = \overline{u^2} f_\eta(n) dn,$$

and

$$\frac{1}{2} \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2} = \frac{\overline{u^2} f_\eta(n) dn}{1 + \left(\frac{2\pi n}{F}\right)^2}.$$

Equation (14) can be expressed as:

$$\overline{u_p^2} = \overline{u^2} \int_0^\infty \frac{f_\eta(n) dn}{1 + \left(\frac{2\pi n}{F}\right)^2}. \quad (15)$$

If function $f_\eta(n)$ is known, Equation (15) can be used to calculate $\overline{u_p^2}$. However, $f_\eta(n)$, the Lagrangian frequency function, is not as well-known as that of the Eulerian [18]. In the following, an approximation was made from R_η , which is measurable.

The relative velocity between the particle and the stream can be represented by:

$$\Delta u = u - u_p. \quad (16)$$

The intensity of turbulence of the particles since relative to the stream can be obtained from:

$$\overline{(\Delta u)^2} = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T (\Delta u)^2 dt. \quad (17)$$

Introducing Eqs. (1), (9) and (16) into Eq. (17), it can be shown that, without any further simplification,

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T (\Delta u)^2 dt &= \frac{1}{2} \sum_n A_n^2 \\ &+ \frac{1}{2} \sum_n \frac{A_n^2}{\left[1 + \left(\frac{2\pi n}{F}\right)^2\right]^2} + \frac{1}{2F^2} \sum_n \frac{(2\pi n)^2 A_n^2}{\left[1 + \left(\frac{2\pi n}{F}\right)^2\right]^2} \\ &- \sum_n \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2} = \frac{1}{2} \sum_n A_n^2 - \frac{1}{2} \sum_n \frac{A_n^2}{1 + \left(\frac{2\pi n}{F}\right)^2}; \end{aligned}$$

or

$$\overline{(\Delta u)^2} = \overline{u^2} - \overline{u_p^2} \quad (18)$$

The Lagrangian correlation of the particle motion can be shown to be:

$$R_t = \frac{\overline{u_p(t) u_p(t+\xi)}}{\overline{u_p^2}} = \frac{\sum_n \frac{A_n^2}{F^2 + (2\pi n)^2} \cos 2\pi n \xi}{\sum_n \frac{A_n^2}{F^2 + (2\pi n)^2}}. \quad (19)$$

In terms of η , substituting $\eta/\sqrt{u^2}$ for ξ in Eq. (19) and postulating as in Eq. (15), the Lagrangian correlation of the particle can be expressed in terms of the Fourier integral:

$$R'_\eta(\eta) = \frac{\int_0^\infty \frac{f_\eta(n)}{1 + \left(\frac{2\pi n}{F}\right)^2} \cos 2\pi n \frac{\eta}{\sqrt{u^2}} dn}{\int_0^\infty \frac{f_\eta(n)}{1 + \left(\frac{2\pi n}{F}\right)^2} dn}. \quad (20)$$

The scale of turbulence of the particles:

$$l'_1 = \int_0^\tau R'_\eta d\eta, \quad (21)$$

$$R'_\eta(\eta) = R'_\eta(\eta'),$$

where

$$\eta' = \sqrt{u_p^3} dt; \quad l_1' = \sqrt{\frac{u_p^3}{u^3}} \int_0^T R_\eta(\eta) d\eta \doteq \int_0^T R_\eta(\eta') d\eta'. \quad (22)$$

Therefore, knowing the Lagrangian correlation (scale) and intensity of one component of the two phases, and the properties of the stream and particle (F), the scale and intensity of turbulence and the correlation of the other phase can be calculated.

Other relations of interest are :

(a) The viscous dissipation due to each particle of mass m can be calculated from : (for three components)

$$W_p = 3 \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T (\text{drag force}) (\Delta u) dt \\ = 3 F m \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T (\Delta u^2) dt,$$

for : Drag force $= Fm (\Delta u)$. From Eq. (18),

$$W_p = 9\pi\mu d_p (\bar{u}^2 - \bar{u}_p^2) \quad (23)$$

(b) The ratio of particle diffusivity to eddy diffusivity, from Einstein's equation of diffusivity, is [2] :

$$\frac{E_p}{E} = \frac{\sqrt{u_p^3} l_1'}{\sqrt{u^3} l_1}. \quad (24)$$

The evaluation of the integrals obtained in the above from the curve of $f_\eta(n)$ analogous to $f(n)$ given in Reference [18] is tedious. The relative magnitude of various quantities and basic parameters affecting momentum transfer can be seen from the following approximate solution :

APPROXIMATE SOLUTION

The curve of

$$R_\eta = e^{-\eta^2/\Lambda_\eta^2}, \quad (25)$$

has the same curvature at the apex as the parabola

$$R_\eta = 1 - \frac{\eta^2}{\Lambda_\eta^2} \quad (26)$$

where Λ_η was explained by TAYLOR as a measure

of smallest eddies responsible for the dissipation of energy. This parabola, in many cases, is a sufficient approximation of R_η .

The curve of $R_\eta(\eta)$ from experiment by TAYLOR is reproduced in Fig. 1 together with curves given in Eqs. (25), (26) for comparison. Use of correlation curve obtained in Reference [2] showed similar type of agreement.

Using the approximation given by Eq. (25), from Eq. (5) :

$$f_\eta(n) = \frac{2\sqrt{\pi}\Lambda_\eta}{\sqrt{u^3}} e^{-\Lambda_\eta^2 \pi^2 n^2 / u^3}, \quad (27)$$

$$\int_0^\infty f_\eta(\eta) d\eta = 1.$$

From eq. (6),

$$l_1 = \frac{\sqrt{\pi}}{2} \Lambda_\eta. \quad (28)$$

From eq. (15),

$$\bar{u}_p^2 = \frac{2\sqrt{\pi}\Lambda_\eta}{\sqrt{u^3}} \int_0^\infty \frac{e^{-\Lambda_\eta^2 \pi^2 n^2 / u^3} dn}{1 + \left(\frac{2\pi n}{F}\right)^2} \\ = \bar{u}^2 \left[1 - \frac{1}{2} K + \frac{8.1}{2^3} K^2 - \frac{5.8.1}{2^5} K^3 + \frac{7.5.8.1}{2^7} K^4 \dots \right],$$

or

$$\bar{u}_p^2 = \bar{u}^2 G(K); \quad G(K) < 1; \quad (29)$$

* It would be interesting to notice that, with the Eulerian system, using the approximation :

$$R_\eta = e^{-\eta^2/\Lambda^2}$$

The corresponding frequency function is :

$$f(n) = \frac{2\sqrt{\pi}\Lambda}{U} e^{-\Lambda^2 \pi^2 n^2 / U^2}, \quad (a)$$

and

$$l_2 = \frac{\sqrt{\pi}}{2} \Lambda. \quad (b)$$

The difference between $f_\eta(n)$ and $f(n)$ can be seen by comparing eqs. (27) and (a). Further, TAYLOR gave :

$$B^2 = \frac{2}{9} \frac{\Lambda^2}{\Lambda_\eta^2} \approx 1$$

or $\Lambda_\eta = 0.5$ and $l \approx 0.5 l$, from eqs. (28) and (b).

where

$$\sqrt{K} = \frac{2\sqrt{u^2}}{F\Lambda_\eta} = \frac{1}{9} \left(\frac{d_p \sqrt{u^2} \rho}{\mu} \right) \left(\frac{d_p}{\Lambda_\eta} \right) \left(\frac{\rho_p}{\rho} \right) = \frac{1}{9} \bar{Re} \left(\frac{d_p}{\Lambda_\eta} \right) \left(\frac{\rho_p}{\rho} \right), \quad (30)$$

from which the factors affecting momentum transfer between the two phases can be observed. The Reynolds number \bar{Re} is the Reynolds number of the particle if the solid particle is held at a uniform velocity equal to the average velocity of the stream. Physically, this root-mean-squared Reynolds number is a characteristic Reynolds number of the viscous drag imparted to the solid particle by the stream to produce oscillatory motion of the particle.

From eq. (20),

$$R_\eta' = \frac{\bar{u}^2}{u_p^2} \frac{2\sqrt{\pi} \Lambda_\eta}{\sqrt{u^2}} \int_0^\infty \frac{e^{-\Lambda_\eta' \pi^2 n^2 / \bar{u}^2}}{1 + \left(\frac{2\pi n}{F} \right)^2} \cos 2\pi \frac{\eta}{\sqrt{u^2}} n \, dn$$

$$= e^{-\eta^2 / \Lambda_\eta'} H(K, \eta / \Lambda_\eta) / G(K), \quad (31)$$

where

$$H\left(K, \frac{\eta}{\Lambda_\eta}\right) = G(K) + \left(\frac{\eta}{\Lambda_\eta}\right)^2 \left(K - 3K^2 + \frac{45}{4}K^3 - \frac{105}{2}K^4 + \dots\right) + \left(\frac{\eta}{\Lambda_\eta}\right)^4 \left(K^2 - \frac{15}{2}K^3 + \frac{105}{2}K^4 - \dots\right) + \left(\frac{\eta}{\Lambda_\eta}\right)^6 (K^3 - 14K^4 + \dots) + \left(\frac{\eta}{\Lambda_\eta}\right)^8 (K^4 - \dots) + \dots$$

The integration formulae for the above transforms are present in Appendix II. From eq. (25),

$$R_\eta' = R_\eta H\left(K, \frac{\eta}{\Lambda_\eta}\right) / G(K), \quad (32)$$

or

$$\frac{\eta^2}{\Lambda_\eta'^2} = \frac{\eta^2}{\Lambda_\eta^2} - \ln H\left(K, \frac{\eta}{\Lambda_\eta}\right) + \ln G(K), \quad (33)$$

from which Λ_η' can be solved, since \bar{u}_p^2 is known from [29]. However, Λ_η' can again be approximated by finding the parabola having the same

curvature at the apex of the $R_\eta'(\eta)$ curve. Expressing $R_\eta'(\eta)$ in terms of:

$$R_\eta' = e^{-\eta^2 / \Lambda_\eta'} \left[1 + \left(\frac{\eta}{\Lambda_\eta}\right)^2 \frac{I(K)}{G(K)} + \dots \right], \quad (31a)$$

$$\left. \frac{d^2 R_\eta'}{d\eta^2} \right|_{\eta=0} = - \frac{2[G(K) - I(K)]}{\Lambda_\eta'^2 [G(K)]^2}, \quad (34)$$

and the curvature at the apex of the characteristic parabola is:

$$\left. \frac{d^2 R_\eta'}{d\eta^2} \right|_{\eta=0} = - \frac{2}{\Lambda_\eta'^2}. \quad (35)$$

Hence

$$\frac{\Lambda_\eta'^2}{\Lambda_\eta^2} = \frac{G(K)}{1 - I(K)/G(K)} > 1 \quad (36)$$

The first few terms of the above expression are

$$\frac{\Lambda_\eta'^2}{\Lambda_\eta^2} = 1 + \frac{K}{2} - \frac{5}{4}K^2 + \frac{49}{4}K^3 - \frac{291}{16}K^4 + \dots \quad (37)$$

The scale of turbulence:

$$l_1' = \frac{\sqrt{\pi}}{2} \Lambda_\eta'. \quad (38)$$

Comparing eqs. (28), (37), and (38), $l_1' > l_1$ in

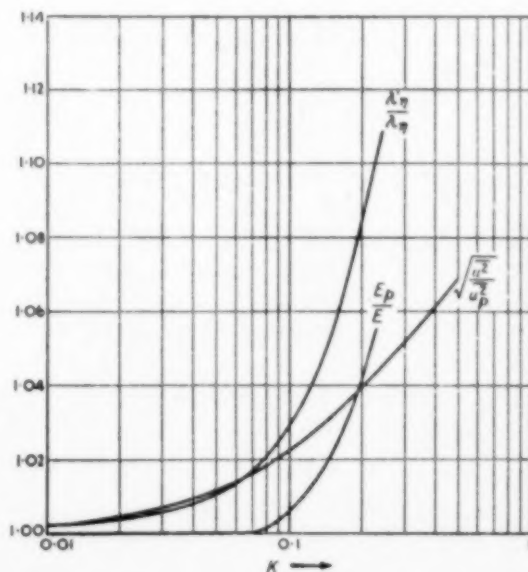


FIG. 2. Ratios of intensities, scales, and diffusivities of particles to those of steam at various K .

general. The ratio of particle diffusivity to eddy diffusivity will simply be, from eq. (24):

$$\frac{E_p}{E} = \frac{A'_p}{A'_e} \sqrt{\frac{u_p^2}{u^2}} = \frac{G(K)}{\sqrt{1-I(K)/G(K)}} > 1. \quad (39)$$

The values of $\sqrt{u^2/u_p^2}$, A'_p/A'_e , and E_p/E for various values of K are as shown in Fig. 2. The relation between $(\Delta u)^2/u^2$ and K is shown in Fig. 3.

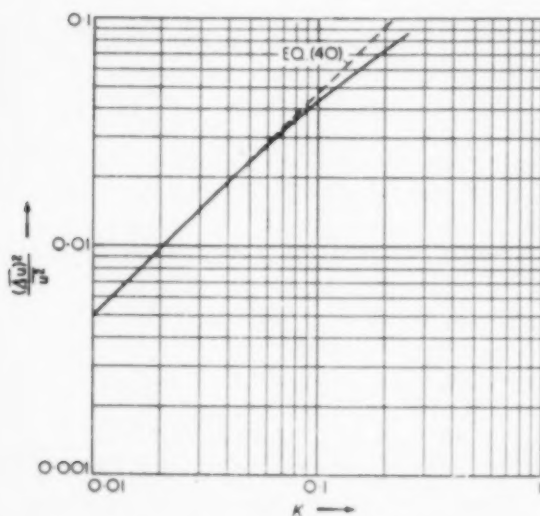


Fig. 3. Ratios of intensities of relative motion between particles and steam to intensities of steam at various K .

DISCUSSION

The above shows that, knowing the intensity and scale of turbulence of one phase of the stream and knowing the properties of the fluid and particles, the intensity and scale of the other phase can be calculated (for small relative motion between the particles and the fluid stream). Where the condition that Re is of order one applies, measurement of one phase of the two, whichever is more convenient to make, suffices.

Functions $G(K)$, $I(K)$ and $H\left(K, \frac{\eta}{A_p}\right)$ obtained from integration of exact statistical frequency function can be tabulated from machine calculations for interpolation from measured quantities.

Figs. 2 and 3 show that the above theoretical results will not apply for large values of K

(eq. (30)). For large values of K , the contribution of the squares and products of the relative velocity between the particle and the stream becomes significant; also, for large values of Re , Stokes's Law will not hold true. Extrapolation could lead to great errors.

From dimensional correlation, it can be shown that:

$$\begin{aligned} \frac{d_p \sqrt{(\Delta u)^2} \rho}{\mu} &= (\text{constant}) \left(\frac{u^2}{g d_p} \right)^{a/2} \left(\frac{d_p \sqrt{u^2} \rho}{\mu} \right)^b \left(\frac{\rho_p}{\rho} \right)^c \left(\frac{l_1}{d_p} \right)^h \\ &= (\text{constant}) (\overline{Fr})^a (\overline{Re})^b \left(\frac{\rho_p}{\rho} \right)^c \left(\frac{l_2}{d_p} \right)^h, \end{aligned} \quad (40)$$

where a , b , c , and h are constants. Comparing with K derived in the above,

$$\sqrt{K} = \frac{\sqrt{\pi}}{18} \left(\frac{d_p \sqrt{u^2} \rho}{\mu} \right) \left(\frac{d_p}{l_1} \right) \left(\frac{\rho_p}{\rho} \right), \quad (30)$$

and for the case of K of order 1/10, it can be approximated that

$$(\Delta u)^2 = u^2 - \bar{u}^2 = \frac{K}{2} u^2 \quad (41)$$

or

$$\frac{d_p \sqrt{(\Delta u)^2} \rho}{\mu} = \frac{\sqrt{\pi}}{18 \sqrt{2}} Re^2 \left(\frac{d_p}{l_1} \right) \left(\frac{\rho_p}{\rho} \right)$$

i.e., in eq. (40) $a = 0$, $b = 2$, $c = 1$, $h = -1$ for this simple case (dash line in Fig. 3). The root-mean-squared Froude number does not come into the above relation due to neglecting the term g^2/F^2 from eq. (13):

$$\begin{aligned} \frac{g^2}{F^2} &= \bar{u}^2 \left(\frac{g d_p}{u^2} \right)^2 \left(\frac{d_p \sqrt{u^2} \rho}{\mu} \right)^2 \left(\frac{\rho_p}{\rho} \right)^2 \\ &= \bar{u}^2 (\overline{Fr})^{-4} (\overline{Re})^2 \left(\frac{\rho_p}{\rho} \right)^2. \end{aligned}$$

The pertinency of neglecting the interaction between the particles for many cases such as in combustion and pneumatic conveying can be seen from the experimental results in Appendix 1, where average distance between the particles is greater than 10 diameters of the particle. However, in the case of fluidization, the particles might be $1\frac{1}{2}$ diameters apart from centre to

centre even for 80% void (Ref. [2]), and the interaction of the particles has to be considered.

It is obvious that in order that the particles can be suspended by a low density stream, the turbulence must be non-decaying and the viscous dissipation of the particles (eq. (23)) must be replenished by the turbulence generated from the boundary layer of the flow duct at the expense of pressure drop. In case of fluidization, the turbulence of the stream is produced by the eddies generated from the particles held down by gravity. Therefore, from the energy consideration, the turbulence existing in the two-phase stream can be calculated. An interesting problem here is the behaviour of the particles in the boundary layer of the stream.

The results obtained in the above can be applied to the following practical cases:

1. To get close proximity to stream flow pattern in the tracer technique, the condition is to choose particles of size and density so to limit the value of K , from estimated flow condition of the stream, to the accuracy required. For instance, to get better than 98% accuracy of the flow pattern, K should be less than .04 as can be seen from eq. (40), (Fig. 8).

2. In pneumatic conveying, the quantity $(\Delta u)^2$ in eq. (23) is significant, as it represents the energy dissipated in suspending the solid particles by turbulent motion. This energy must be replenished by the blower besides the energy in accelerating the particles and the energy dissipated by pipe friction [5].

3. In the combustion of dispersed solid or liquid fuels, the design of the combustion chamber affects greatly the diffusion of fuel particles. It can be seen from the above that to get high particle diffusivity, the scale of turbulence should not be too large and therefore a number of small combustion chambers of reasonable size for proper mixing should be used instead of a single large combustion chamber, and excessive atomization should not be attempted (to maintain large d_p/λ_0 or large K , Fig. 2).

4. In the fluidization of beads of catalyst, although the desirability of large surface area favours small size of beads, particle diffusivity

(Fig. 2), however, favours large size beads; an optimum design can be achieved through the use of beads of suitable size. In other words, large relative motion between the beads and the fluid stream is desirable (Fig. 3).

CONCLUSIONS

1. In a two-phase stream the characteristics of turbulence of one phase can be determined from that of the other phase.
2. The fundamental parameters affecting the statistical properties of momentum transfer between the two phases are:

$$\left(\frac{d_p \sqrt{u^3} \rho}{\mu}\right), \left(\frac{d_p}{l_1}\right), \left(\frac{\rho_p}{\rho}\right).$$

3. When gravity effect of the particles is significant, the turbulent motion of the particles is anisotropic, even though the stream is isotropic. The parameters affecting momentum transfer will then be:

$$\left(\frac{\sqrt{u^3}}{\sqrt{d_p g}}\right), \left(\frac{d_p \sqrt{u^3} \rho}{\mu}\right), \left(\frac{d_p}{l_1}\right), \left(\frac{\rho_p}{\rho}\right).$$

4. In general, the scale of turbulence of the particles is greater than that of the stream; the intensity of the particles is less than that of the stream; and the diffusivity of the particles is greater than the eddy diffusivity of the stream, but tends to the eddy diffusivity of the stream.

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APPENDIX I

Carrying Capacity of an Isotropic Turbulent Fluid Stream—The approximate relation for calculating the carrying capacity of a turbulent stream was developed as follows: TAYLOR gave the energy of turbulence of a fluid stream as: (8)

$$\frac{\rho}{2} (3 \bar{u}^2)$$

In suspending the particles in a two-phase stream, only 1/6 of $3 \bar{u}^2$ is effective, when the intersection of the particles is neglected. For a duct of cross-sectional area A

and length L , the energy available for suspending the particles will be, approximately

$$\frac{\rho L A}{4} u^3$$

Since only the components of u greater than the terminal velocity, V_t , of the particles will be effective and

$$V_t = \frac{d_p^2 g (\rho_p - \rho)}{18 \mu}$$

To suspend N particles, each of mass m , the energy required will be :

$$N m V_t^2 = \frac{M (\Delta t)}{2} V_t^2$$

where M is the particle feed rate ; $\Delta t = \frac{L}{U}$, and U is the average velocity of flow.

$$M = \frac{\rho A U}{4} x^2 \frac{\bar{u}^2}{V_t^2}$$

where x is the percentage of $\frac{u}{\sqrt{u^2}}$ greater than $\frac{V_t}{\sqrt{u^2}}$ and the probable value of x is given in Fig. 4, obtained from statistical velocity distribution developed from kinetic theory of gases [14].

HALLSTROM [15] measured experimentally the maximum carrying capacity without build-up of a turbulent stream in a 3 in. diameter duct at various average stream velocities, using glass beads of sizes from 105-123 microns in diameter. The intensity of the stream can be calculated from the above equation with the aid of Fig. 4 :

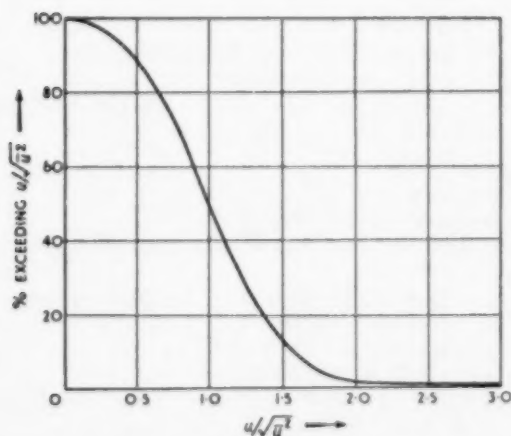


FIG. 4. Probable velocity distribution.

Measured Quantities		Calculated Quantities			
U fps	M lbs/min	Air flow rate, lbs/min	$\sqrt{u^2}/U$	Particles in ³	Mean distance between particles, diameters
20.2	0.727	5.07	.13	1420	21
28.8	1.26	6.22	.132	2230	17
34.8	3.12	6.75	.134	4570	14

APPENDIX II

Integration Formula Developed for the Approximate Solution

$$\int_0^\infty \frac{e^{-a^2 n^2}}{1 + b^2 n^2} dn = \int_0^\infty e^{-a^2 n^2} (1 - b^2 n^2 + b^4 n^4 - b^6 n^6 + b^8 n^8 \dots) dn$$

$$= \frac{\sqrt{\pi}}{2a} \left[1 - \frac{b^2}{2a^2} + \frac{1 \cdot 3}{2^2} \frac{b^4}{a^4} - \frac{1 \cdot 3 \cdot 5}{2^3} \frac{b^6}{a^6} + \frac{1 \cdot 3 \cdot 5 \cdot 7}{2^4} \frac{b^8}{a^8} \dots \right]$$

$$= G(b^2/a^2) \cdot \sqrt{\pi}/2a$$

$$\int_0^\infty \frac{e^{-a^2 n^2}}{1 + b^2 n^2} \cos 2pn \, dn = \int_0^\infty e^{-a^2 n^2} (1 - b^2 n^2 + b^4 n^4 - b^6 n^6 + b^8 n^8 \dots) \cos 2pn \, dn$$

$$= F_0 - b^2 F_2 + b^4 F_4 - b^6 F_6 + b^8 F_8 \dots$$

where

$$F_0 = \frac{\sqrt{\pi}}{2a} e^{-p^2/a^2}$$

$$F_2 = \left(\frac{1}{2a^2} - \frac{p^2}{a^4} \right) F_0$$

$$F_4 = \left(\frac{3}{2a^2} - \frac{p^2}{a^4} \right) F_2 - \frac{p^2}{a^6} F_0$$

$$F_6 = \left(\frac{5}{2a^2} - \frac{p^2}{a^4} \right) F_4 - \frac{2p^2}{a^6} F_2 - \frac{2p^2}{a^8} F_0$$

$$F_n = \left(\frac{n-1}{2a^2} - \frac{p^2}{a^4} \right) F_{n-2} - \left(\frac{n-1}{2} \right) \frac{p^2}{a^6} F_{n-4} -$$

$$\left(\frac{n-1}{2} \right) \frac{n-2}{2} \frac{p^2}{a^8} F_{n-6}$$

centre even for 80% void (Ref. [2]), and the interaction of the particles has to be considered.

It is obvious that in order that the particles can be suspended by a low density stream, the turbulence must be non-decaying and the viscous dissipation of the particles (eq. (23)) must be replenished by the turbulence generated from the boundary layer of the flow duct at the expense of pressure drop. In case of fluidization, the turbulence of the stream is produced by the eddies generated from the particles held down by gravity. Therefore, from the energy consideration, the turbulence existing in the two-phase stream can be calculated. An interesting problem here is the behaviour of the particles in the boundary layer of the stream.

The results obtained in the above can be applied to the following practical cases:

1. To get close proximity to stream flow pattern in the tracer technique, the condition is to choose particles of size and density so to limit the value of K , from estimated flow condition of the stream, to the accuracy required. For instance, to get better than 98% accuracy of the flow pattern, K should be less than .04 as can be seen from eq. (40), (Fig. 8).

2. In pneumatic conveying, the quantity $(\Delta u)^2$ in eq. (23) is significant, as it represents the energy dissipated in suspending the solid particles by turbulent motion. This energy must be replenished by the blower besides the energy in accelerating the particles and the energy dissipated by pipe friction [5].

3. In the combustion of dispersed solid or liquid fuels, the design of the combustion chamber affects greatly the diffusion of fuel particles. It can be seen from the above that to get high particle diffusivity, the scale of turbulence should not be too large and therefore a number of small combustion chambers of reasonable size for proper mixing should be used instead of a single large combustion chamber, and excessive atomization should not be attempted (to maintain large d_p/λ_η or large K , Fig. 2).

4. In the fluidization of beads of catalyst, although the desirability of large surface area favours small size of beads, particle diffusivity

(Fig. 2), however, favours large size beads; an optimum design can be achieved through the use of beads of suitable size. In other words, large relative motion between the beads and the fluid stream is desirable (Fig. 3).

CONCLUSIONS

1. In a two-phase stream the characteristics of turbulence of one phase can be determined from that of the other phase.
2. The fundamental parameters affecting the statistical properties of momentum transfer between the two phases are:

$$\left(\frac{d_p \sqrt{u^2} \rho}{\mu}\right), \left(\frac{d_p}{l_1}\right), \left(\frac{\rho_p}{\rho}\right).$$

3. When gravity effect of the particles is significant, the turbulent motion of the particles is anisotropic, even though the stream is isotropic. The parameters affecting momentum transfer will then be:

$$\left(\frac{\sqrt{u^2}}{\sqrt{d_p g}}\right), \left(\frac{d_p \sqrt{u^2} \rho}{\mu}\right), \left(\frac{d_p}{l_1}\right), \left(\frac{\rho_p}{\rho}\right).$$

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where M is the particle feed rate ; $\Delta t = \frac{L}{U}$, and U is the average velocity of flow.

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where x is the percentage of $\frac{u}{\sqrt{u^2}}$ greater than $\frac{V_t}{\sqrt{u^2}}$ and the probable value of x is given in Fig. 4, obtained from statistical distribution developed from kinetic theory of gases [14].

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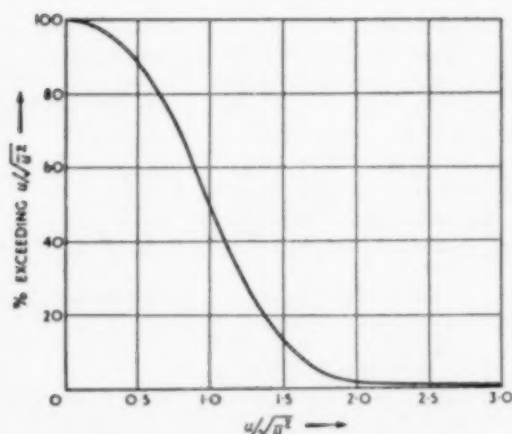


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$$= \frac{\sqrt{\pi}}{2a} \left[1 - \frac{b^2}{2a^2} + \frac{1.3}{2^2} - \frac{b^4}{a^4} + \frac{1.3.5}{2^3} \frac{b^6}{a^6} - \frac{1.3.5.7}{2^4} \frac{b^8}{a^8} \dots \right]$$

$$= G(b^2/a^2) \cdot \sqrt{\pi}/2a$$

$$\int_0^\infty \frac{e^{-a^2 n^2}}{1 + b^2 n^2} \cos 2pn \, dn = \int_0^\infty e^{-a^2 n^2} (1 - b^2 n^2 + b^4 n^4 - b^6 n^6 + b^8 n^8 \dots) \cos 2pn \, dn$$

$$= F_0 - b^2 F_2 + b^4 F_4 - b^6 F_6 + b^8 F_8 \dots$$

where

$$F_0 = \frac{\sqrt{\pi}}{2a} e^{-p^2/a^2}$$

$$F_2 = \left(\frac{1}{2a^2} - \frac{p^2}{a^4} \right) F_0$$

$$F_4 = \left(\frac{3}{2a^2} - \frac{p^2}{a^4} \right) F_2 - \frac{p^2}{a^6} F_0$$

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$$F_n = \left(\frac{n-1}{2a^2} - \frac{p^2}{a^4} \right) F_{n-2} - \left(\frac{n-1}{2} \right) \frac{p^2}{a^6} F_{n-4} -$$

$$\left(\frac{n-1}{2} \right) \frac{n-2}{2} \frac{p^2}{a^8} F_{n-6}$$

$$\begin{aligned}
& - \frac{\left(\frac{n-1}{2}\right) \left(\frac{n-2}{2}\right) \left(\frac{n-3}{2}\right)}{a^{10}} p^3 P_{n-8} \dots \\
& - \frac{\left(\frac{n-1}{2}\right)!}{2!} \frac{p^3}{a^{n-3}} P_4 \\
& - \frac{\left(\frac{n-1}{2}\right)!}{1!} \frac{p^2}{a^n} F_2 - \left(\frac{n-1}{2}\right)! \frac{p^2}{a^{n+2}} F_0
\end{aligned}$$

The general form of the above integral is

$$\begin{aligned}
\int_0^\infty \frac{e^{-a^2 n^2}}{1+b^2 n^2} \cos 2pn \, dn &= \frac{\sqrt{\pi}}{2a} e^{-p^2/a^2} \\
& \left[\left(1 - \frac{1}{2} \frac{b^2}{a^2} + \frac{1 \cdot 3}{2^2} \frac{b^4}{a^4} - \frac{1 \cdot 3 \cdot 5}{2^3} \frac{b^6}{a^6} + \frac{1 \cdot 3 \cdot 5 \cdot 7}{2^4} \frac{b^8}{a^8} \dots \right) \right. \\
& + \frac{p^2}{a^2} \left(\frac{b^2}{a^2} - \frac{3 \cdot 2}{2^2} \frac{b^4}{a^4} + \frac{8 \cdot 5 \cdot 2 \cdot 3}{2^3} \frac{b^6}{a^6} - \frac{3 \cdot 5 \cdot 7 \cdot 2 \cdot 3 \cdot 4}{2^4} \frac{b^8}{a^8} + \dots \right) \\
& + \frac{p^4}{a^4} \left(\frac{b^4}{a^4} - \frac{5 \cdot 3}{2^2} \frac{b^6}{a^6} + \frac{5 \cdot 7 \cdot 3 \cdot 4}{2^3} \frac{b^8}{a^8} - \frac{5 \cdot 7 \cdot 9 \cdot 3 \cdot 4 \cdot 5}{2^4} \frac{b^{10}}{a^{10}} + \dots \right) \\
& + \frac{p^6}{a^6} \left(\frac{b^6}{a^6} - \frac{7 \cdot 4}{2^2} \frac{b^8}{a^8} + \frac{7 \cdot 9 \cdot 4 \cdot 5}{2^3} \frac{b^{10}}{a^{10}} - \frac{7 \cdot 9 \cdot 11 \cdot 4 \cdot 5 \cdot 6}{2^4} \frac{b^{12}}{a^{12}} + \dots \right) \\
& + \frac{p^8}{a^8} \left(\frac{b^8}{a^8} - \frac{9 \cdot 5}{2^2} \frac{b^{10}}{a^{10}} + \frac{9 \cdot 11 \cdot 5 \cdot 6}{2^3} \frac{b^{12}}{a^{12}} - \frac{9 \cdot 11 \cdot 13 \cdot 5 \cdot 6 \cdot 7}{2^4} \frac{b^{14}}{a^{14}} + \dots \right) \\
& + \frac{p^{10}}{a^{10}} \left(\frac{b^{10}}{a^{10}} - \frac{11 \cdot 6}{2^2} \frac{b^{12}}{a^{12}} + \frac{11 \cdot 13 \cdot 6 \cdot 7}{2^3} \frac{b^{14}}{a^{14}} - \dots \right) + \dots \Big] \\
&= \frac{\sqrt{\pi}}{2a} e^{-p^2/a^2} H \left(\frac{p^2}{a^2}, \frac{b^2}{a^2} \right) \\
&= \frac{\sqrt{\pi}}{2a} e^{-p^2/a^2} \left[G \left(\frac{b^2}{a^2} \right) + \frac{p^2}{a^2} I \left(\frac{b^2}{a^2} \right) + \dots \right]
\end{aligned}$$

NOTATIONS

(with dimensions of each quantity in mass, M ; length, L ; and time, T)

- A_n = amplitude of the n th harmonic of velocity fluctuation, LT^{-1}
 C_D = drag coefficient, dimensionless
 d_p = diameter of particle, L
 E = eddy diffusivity, $L^2 T^{-1}$
 E_p = diffusivity of the particle, $L^2 T^{-1}$
 $F = 18 \mu (d_p^3 \rho_p)^{-1} T^{-1}$
 $f(n)$ = Eulerian statistical frequency function, T
 $f_\eta(n)$ = Lagrangian statistical frequency function, T
 Fr = root-mean-squared Froude number $\sqrt{u^2/d_p g}$, dimensionless
 $G(K)$ = function of K defined by eq. (29), dimensionless
 g = Gravitational acceleration, LT^{-2}

$I(K)$ = function of K defined by eq. (31a), dimensionless

K = defined by eq. (30), dimensionless

k = an empirical constant

l_1 = Lagrangian scale of turbulence of the stream, L

l_1' = Lagrangian scale of turbulence of the particle, L

l_2 = Eulerian scale of turbulence, L

m = mass of a particle, M

n = frequency, T^{-1}

R_s = Eulerian correlation of the stream motion, dimensionless

R_l = Lagrangian correlation of the stream motion, dimensionless

R_η = Lagrangian correlation of the stream motion, based on η , dimensionless

$R_{\eta'}$ = Lagrangian correlation of the particle motion, based on η or η' , dimensionless

Re = Reynolds number of particle, dimensionless

Re = root-mean-squared Reynolds number, $\frac{d_p \sqrt{u^2} \rho}{\mu}$, dimensionless

T = long time interval, T

t = time, T

u = axial component of turbulent velocity component of the stream, LT^{-1}

v = vertical component of turbulent velocity of the stream, LT^{-1}

u_p = Axial component of turbulent velocity of the particle, LT^{-1}

v_p = vertical component of turbulent velocity of the particle, LT^{-1}

Δu = relative velocity between the particle and the stream, LT^{-1}

$\overline{u^2}$ = intensity of turbulence of the stream, $L^2 T^{-2}$

$\overline{u_p^2}$ = axial intensity of turbulence of the particle, $L^2 T^{-2}$

$\overline{v_p^2}$ = vertical intensity of turbulence of the particle, $L^2 T^{-2}$

$(\Delta u)^2$ = intensity of the particle relative to the stream, $L^2 T^{-2}$

W_p = viscous dissipation of the particle, per unit time, $ML^2 T^{-3}$

x = measured in the axial direction of flow, L

$\overline{X^2}$ = average displacement, L^2

θ_n = angle of phase lag of velocity of particle from the stream, dimensionless

η = defined by $d\eta = \sqrt{u^2} dt$, L

η' = defined by $d\eta' = \sqrt{u_p^2} dt$, L

Λ = defined in reference [7]

Λ_η = defined by eq. (7), a measure of size of eddy of the stream, L

Λ'_η = a quantity analogous to Λ_η , but for the particle, L

μ = viscosity of the stream, $ML^{-1} T^{-1}$

ρ = density of the stream, ML^{-3}

ρ_p = density of the particle, ML^{-3}

ξ = time measure, T

(Note—Notations in the Appendices are explained in the Appendices.)

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Heat transfer to boiling binary liquid mixtures

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Abstract—Heat transfer in boiling liquid mixtures of water and methylethylketone has been measured throughout the ranges of convection and nucleate boiling at atmospheric pressure [43]. With some mixtures a considerably higher maximum heat flux in nucleate boiling has been found than in the case of water. This higher heat flux is obtained at the same temperature of the heating surface as for water, or alternatively, the same heat flux is obtained at a lower surface temperature.

For mixtures of water with acetone, methylethylketone, the lower aliphatic alcohols and ethyleneglycol respectively, the maximum heat flux in nucleate boiling has been studied as a function of concentration. In addition, mixtures consisting of two organic liquids, i.e. dioxane-methanol and 2-chloroethanol—di-iso-propylether, were investigated. In all mixtures a maximum value of the maximum heat flux for nucleate boiling occurs at a certain concentration. The higher the number of carbon atoms in the alcohol and ketone series, the more this maximum is shifted towards lower concentrations of the organic component. A maximum of 3½ times the value for water has been observed in the system water—1-pentanol. Partial miscibility has no influence on the continuity of the maximum heat transfer curve.

The occurrence of the maximum is qualitatively explained by the higher dew point of the vapour formed by flash vaporization, as compared with the boiling point of the original liquid mixture. At a certain concentration, the dew point of the vapour bubbles may become equal to the temperature of the surrounding superheated liquid, and in that case the vapour bubbles grow only by diffusional mass transfer. The average size of the bubbles leaving the heating surface is then smaller, and the maximum heat transfer is higher. For mixtures of water and alcohols, it has been calculated that 1 mole % of the liquid is immediately vaporized at the surface. For water—acetone and water—methylethylketone, only 0.3 and 0.1 mole % direct vaporization respectively is found.

Résumé—Les auteurs ont étudié et mesuré le transfert de chaleur dans des mélanges à l'ébullition d'eau et de méthyléthylcétone (43) d'un bout à l'autre de l'intervalle convection - nucleate boiling.

Pour certains mélanges ils ont trouvé un maximum du flux de chaleur dans le "nucleate boiling" considérablement plus élevé que dans le cas de l'eau. Ce flux de chaleur plus élevé est obtenu pour la même température de surface chauffante que dans le cas de l'eau ou réciproquement le même flux de chaleur s'obtient avec une température de surface plus faible.

Dans le cas de mélanges d'eau et d'écétone, de méthyléthylcétone, d'éthylène glycol et d'alcools aliphatiques inférieurs respectivement, les auteurs ont étudié le maximum du flux de chaleur dans le "nucleate boiling" en tant que fonction de la concentration. En outre, ils ont expérimenté des mélanges de deux liquides organiques, par exemple: dioxane - méthanol et 2-chloroéthanol-di-iso-propylethyléther. Pour certaines concentrations, le flux de chaleur maximum pour le "nucleate boiling" présente un maximum. Plus le nombre d'atomes de C est grand dans les alcools et cétones, plus le maximum est déplacé vers les concentrations faibles en composant organique. La valeur de ce maximum atteint trois fois et demi la valeur observée avec l'eau, dans le cas du système eau-pentanol. La miscibilité partielle est sans influence sur la continuité de la courbe du transfert de chaleur maximum.

La production de ce maximum s'explique qualitativement par le fait que le point de rosée de la vapeur formée par vaporisation instantanée est plus élevé que le point d'ébullition du mélange liquide primitif.

A une certaine concentration le point de rosée des bulles de vapeur peut devenir égal à la température du liquide surchauffé environnant et dans ce cas, les bulles de vapeur ne croissent

que par transfert de masse par diffusion. La dimension moyenne des bulles quittant la surface chauffante est alors plus petite et le transfert maximum de chaleur est plus élevé. Pour des mélanges d'eau et d'alcools, les auteurs ont calculé qu'une mole % de liquide est immédiatement vaporisée à la surface, pour les mélanges eau-acétone et eau-méthyléthylcétone ils n'ont trouvé que 0,3 et 0,1% moles directement vaporisées.

GENERAL SURVEY

Heat transfer to boiling liquids has been the subject of many investigations. It is discussed in current textbooks, e.g. of McADAMS [33] and of JAKOB [20].

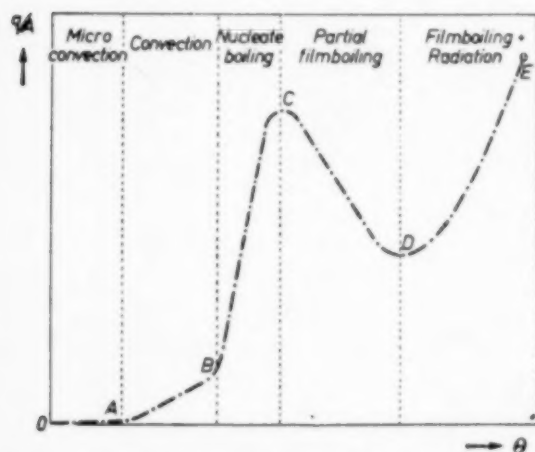


FIG. 1. Schematic representation of heat flux q/A as a function of temperature difference θ between heating surface and bulk of liquid.

The curve showing heat flux q/A as a function of temperature difference θ between heating surface and bulk of liquid is schematically given in Fig. 1. Five regions can be distinguished, the first of which is OA in which heat is transferred by convection (and also by conduction), and no vapour bubbles are observed. This also holds true for the region AB . The convection in the latter region is, however, much more intense than in the region OA . We are, therefore, inclined to speak of "micro"-convection in the region OA as distinct from "macro"-convection in AB . At point B formation of bubbles starts on special spots of the heating surface, and nucleate boiling takes place in the region BC . The number of nuclei at which vapour bubbles are generated, and thus the fraction of the surface covered with vapour bubbles, increases in the region B to C ,

until in the region CD a gradually increasing area of the heating surface is covered with a coherent layer of vapour. At the same time the heat flux drops as a result of the presence of the insulating vapour layer, although the temperature difference θ between heating wire and bulk liquid increases. Thereafter the heat flux rises again, owing to the increasing contribution of radiation, until the wire burns out at E .

Nucleate boiling heat transfer has been investigated extensively and mostly for water. The maximum at C (Fig. 1) has been mentioned by several authors, mainly for water [4, 7, 11, 23, 24, 34, 37, 41].

Comparatively little work has been done on mixtures. BONILLA and PERRY [4] have investigated some binary mixtures of water with ethanol, acetone and butanol respectively, as well as binary mixtures of ethanol—butanol and ethanol—acetone. CICHELLI and BONILLA [7] have investigated mixtures of water—ethanol and propane—n-pentane; BONILLA and EISENBERG [5] water—styrene and water—butadiene; BONETT and GESTER [13] hydrocarbons—furfural; KIRSCHBAUM water—ethanol, benzene—toluene [28] and water—glycerol [29].

In a narrow concentration range in which water was present in excess, experiments were made by CRYDER and GILLILAND [9] on glycerol, saccharose, NaCl , Na_2SO_4 ; by CRYDER and FINALBORGO [8] on glycerol, Na_2SO_4 ; by LARSON [30] on NaOH , CaCO_3 ; by RHODES and BRIDGES [41] on oleic acid with NaCl and Na_2CO_3 ; by INSINGER and BLISS [18], JAKOB and LINKE [24], KIRSCHBAUM [29] and MORGAN *et al.* [36] on wetting agents; by McADAMS *et al.* [35] on air.

In some of their mixtures BONILLA and PERRY have found a maximum heat flux in nucleate boiling (at point C in Fig. 1) exceeding somewhat that of either one of the pure components [4]. No systematic investigation about the influence of concentration was, however, made, and the increase of maximum heat flux mentioned by them was very moderate.

KIRSCHBAUM [29] has found that in 20% by weight solution of glycerol in water the overall coefficient of heat transfer was twice as high as with pure water, or as in a 50% by weight solution of glycerol, at the same temperature difference $\theta = 20^\circ\text{C}$. He attributes this behaviour to foaming. No sufficient data are, however, given to conclude that the maximum heat flux was reached in this case.

Table 1. Survey of data at atmospheric pressure concerning points

Component		Boiling point			Azeotrope				Solubility		
A	B	T_A	T_B	T_{Az}	%B		$T_A - T_{Az}$	Reference	g/100g	Wt	T
					Wt	Mole					
water	ethanol	100	78.3 78.3	78.15 78.13	95.57 95.59	89.41 89.45	21.85 21.87	17, 27, 31 31	~	~	
"	1-propanol	100	97.2 97.19 97.2	87.72 87.72 87.75	71.69 71.69 71.95	43.17 43.17 43.49	12.28 12.28 12.35	17 31 31	~	~	
"	t-butanol	100	82.55	79.91 79.96	88.24 90.8	64.60 70.8	20.09	17, 31 31	~	~	
"	1-butanol	100	117.75 117.6 116.9 117.70	92.4 92.4 92.25 92.50	62 62 63 57.5	28.4 28.4 29.3 24.76	7.6 7.6 7.75 7.50	17 17, 31 31 26, 27	7.9	7.9 7.81 7.09 7.4	90 20 20 23
"	1-pentanol	100	187.6 187.6 187.7 188.0	95.95 95.95 95.4 96.0	46 46.6 46 46.0	14.8 15.1 14.8 14.8	4.05 4.05 4.6 4.0	17 31 31 31	2.7 2.26	3.65 3.39	27 24
"	1-hexanol	100	157.85	97.8	25	5.54	2.2	17	0.628 0.59	0.505 0.534	21 26
"	1-heptanol	100	176.15	98.7	17	3.08	1.8	17	0.280 0.180 0.09	0.344 0.1275 0.0340	10 2 1
"	1-octanol	100	195.15 195.15	99.4 99.5	10 11	1.5 1.7	0.6 0.5	17, 31 31	0.0558	0.0745	2
"	acetone	100	56.4 56.50	non-azeotrope non-azeotrope				17, 31 27		~	~
"	methylethylketone	100	79.6 79.6 79.56 79.60 79.6 79.6	73.45 73.45 73.37 73.6 73.8 73.6	89 88.6 88.62 89.1 89	66.9 66.0 66.07 67.1 66.9	26.55 26.55 26.43 26.4 26.7 26.4	17 31 31 27 28 32	19 85.8	15.94 15.75 18.09 22.67 26.01 26.57 33.68 90.1 87.58	9 8 7 2 1 2 6 2 1
dioxane	methanol	101.4 101.05	64.7 64.90	non-azeotrope non-azeotrope				17 27	~	~	
2-chloroethanol	di-iso-propylether	128 128.00	68.5 68.40	non-azeotrope non-azeotrope				17 27	~	~	
ethyleneglycol	water (747 mm)	196.70 197.65 197.4	99.90 100 100	non-azeotrope non-azeotrope non-azeotrope				27 17 17, 31	~	~	
1-butanol	water										
1-pentanol	water										

In systems for which no complete equilibrium data are known, the equilibrium constant has been estimated from the ratio of its value to the value for component A are given. The experimental data are given in parentheses.

Heat transfer to boiling binary liquid mixtures

g point, azeotrope, solubility and maximum heat flux.

A		Maximum K	Heat flux (q/A) max			Data at max. (q/A) max				Data at theor. max for G selected				Selected G
Temp.	Ref.		Max	A	Ratio	T	K	%B		T	K	%B		
								Wt	Mole			Wt	Mole	
		10.2	80	18	1.7	86	4.8	20	9	91.7	7.2	10	4	0.01
		11.6	34	17.0	1.9	89.2	5.1	18	7	98	10.7	6	2	0.01
			43	20	2.2			2.4	0.6					
90 20 20 25 92 90 20	19 15, 19 16, 40 42 18 19 15, 19	24.7 (> 15)	43	17.6	2.5	97.25	21.5	1.6	0.4	95.5	19.5	3	0.75	0.01
22 25	16 40	(> 82)	55	16	3.4			1.8	0.35					
25 20	40 16	(> 58)												
100 28 18	16, 40 40 16	(> 120)												
25	40	(> 205)	28	13.5	1.7	(99.7)		0.35	0.05					
~		28	28	12.8	1.8	78	14.5	12	4	84.8	24	7	2.8	0.008
90 80 78-6 20 10 20 80 20 20	16, 40 19 32 19 16, 40 39 19 19 39	48 (> 15)	41	17.7	2.3	89	87.8	4	1.0	88	84	5	1.8	0.001
		14	15.6	12.4	1.3	73	9.7	2	5	75	9.7	2	5	
		39	22.6	11.7	1.9	90.7	11.6	8	6.5	110.5	81	2	1.5	
		10	21.7	17	1.3	174	9	2	7	171	8.3	2.5	8	
		16.5	18	11	1.2	100	1.7	6	21	111.4	4.7	1	4	
			11	8.5	1.3			4	16.5					

the relation $K = y_{A2}/x_{sm}$. The maximum of maximum heat flux in nucleate boiling for mixtures, and maximum are compared with their values predicted by theory.

In the present article the authors have systematically investigated the influence of concentration upon the maximum heat flux in nucleate boiling. VOS and VAN STRALEN [43] had previously found that for some mixtures of water and methylethylketone a maximum heat flux occurs equal to twice that of water.

The present experiments were carried out at atmospheric pressure with the same boiling vessel as described previously [43], but the horizontal platinum wires (purity 99.99%, diameter 0.02 cm and length about 6 cm) were heated with alternating current. The temperature difference between wire and bulk liquid was not measured. Only the voltage and the current through the heating wire were measured in order to determine the rate of heat transfer q .

Mixtures of water with acetone and methylethylketone, of water with ethanol, 1-propanol, t-butanol, 1-butanol, 1-pentanol and 1-octanol respectively, and of water with ethyleneglycol have been investigated. Experiments were also made with binary mixtures consisting of two organic liquids, i.e. dioxane-methanol and 2-chloroethanol-di-iso-propylether.

Distilled water was used in all cases. The methylethylketone and the 1-pentanol were chemically pure, the latter furfural free, the 1-butanol had a boiling range of 115 to 117°C, and the other liquids were of commercial grade.

The data of mutual solubility at room temperature were taken from International Critical Tables [19], from HODGMAN [16] and from PERRY [40]. The solubilities at the azeotropic boiling point are only known for mixtures of water-methylethylketone [16, 19, 32, 40] and water-1-butanol [15, 19]. The boiling and equilibrium data of the mixtures were taken from literature [26, 27, 40] and further: ethanol [23], 1-butanol [42], methylethylketone [8, 32, 38, 29]. Data pertaining to t-butanol, 1-pentanol and 1-octanol have not been found. Azeotropic data have also been taken from references [17, 31]. A summary of these data is shown in Table 1.

RESULTS

Mixtures of water-methylethylketone and water-acetone

Some measurements have been described in another paper [43]. The curves showing the heat flux q/A as a function of the temperature differ-

ence θ between heating surface and bulk liquid for boiling mixtures of water and methylethylketone are represented in Fig. 2. The mixtures with 4.2 and 88.5% by weight methylethylketone are homogeneous, those with 20% and 52% are in the heterogeneous region.

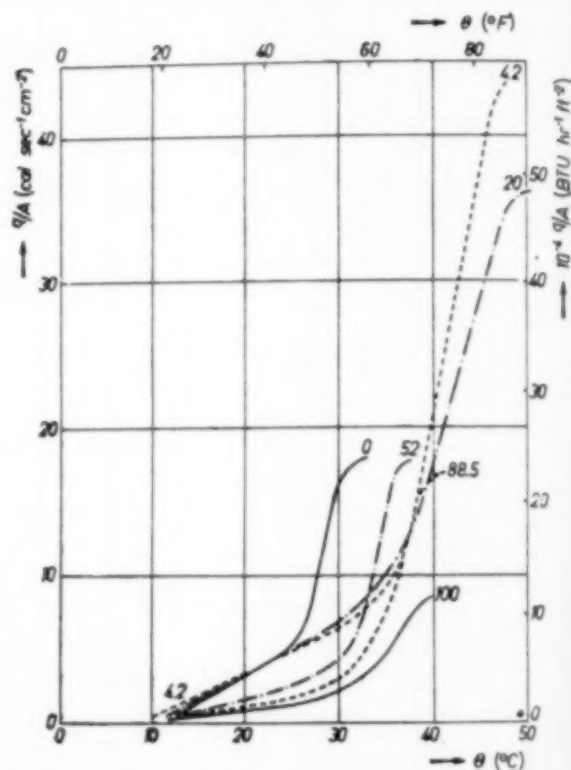


FIG. 2. Water-methylethylketone. Heat flux q/A for convection and nucleate boiling as a function of temperature difference θ between heating surface and liquid. The figures near the curves denote % by weight methylethylketone.

Micro-convection occurs below $\theta = 10^\circ\text{C}$ approximately; at a higher temperature difference a stronger convection sets in until the first visible vapour bubbles occur at $\theta = 25^\circ\text{C}$ approximately. The measurements were continued until filmboiling started. In some cases the wire burned out. The size of the bubbles leaving the heating surface is definitely smaller for 4.2% methylethylketone than with the other mixtures or with the pure components.

The maximum heat flux (at point C in Fig. 1), which forms the separation between the regions of nucleate boiling and filmboiling, differs considerably for different concentrations. It is highest for the mixture containing 4.2% methylethylketone and it is then 150% higher than for pure water.

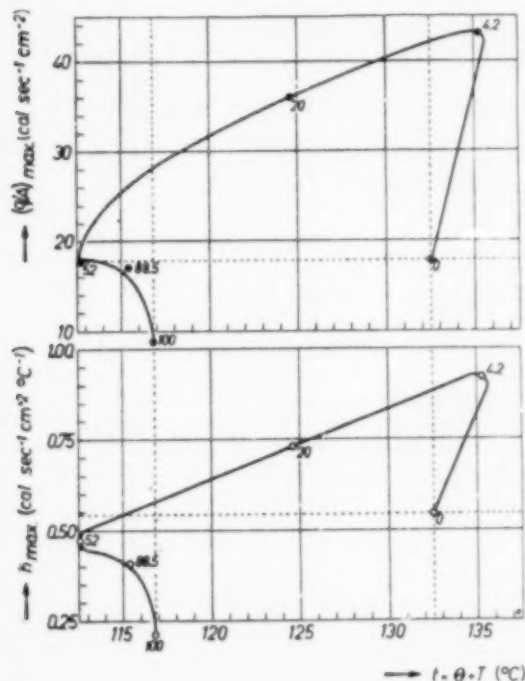


FIG. 3. Water—methylethylketone. Maximum heat flux q/A and maximum coefficient of heat transfer $h = q/A\theta$ for nucleate boiling as a function of temperature $t = \theta + T$ of heating surface. The figures near the circles on the curves denote % by weight methylethylketone. The dotted lines serve for a comparison of the mixtures with the pure components.

The maximum heat flux q/A and the maximum coefficient of heat transfer $h = q/A\theta$ are represented in Fig. 8 as a function of the temperature of the heating wire $t = \theta + T$, where T denotes the boiling temperature of the liquid. The maximum heat flux which is $2\frac{1}{2}$ times the value for water occurs approximately at the same temperature of the wire as with pure water. In another mixture containing approximately 50% methylethylketone the maximum heat flux is equal to that of water but the temperature of the

wire is approximately 20°C lower since the boiling temperature T is approximately 75°C . This mixture consists of two liquid phases.

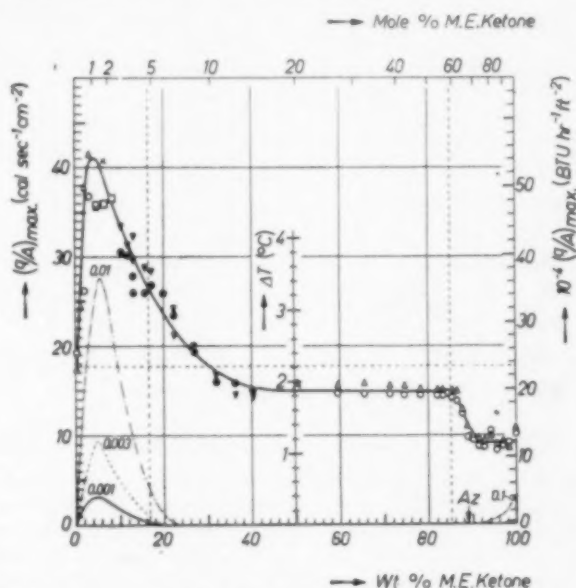


FIG. 4. Water—methylethylketone. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope. The dotted vertical lines indicate the boundaries of the region of demixing at azeotropic boiling point. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

Maximum heat flux as a function of liquid composition is shown in Fig. 4. The dotted vertical lines denote the boundaries of the region of demixing. It is interesting to observe that no discontinuity is found in maximum heat transfer when demixing occurs. Some data concerning $(q/A)_{\max}$ are shown in Table 1, where a comparison with other binary mixtures is also made.

Corresponding measurements for the system water—acetone are represented in Fig. 5. A less pronounced maximum appears at about 12% by weight acetone. A second maximum is observed at a higher concentration. This maximum cannot be explained by the theory which will be given below.

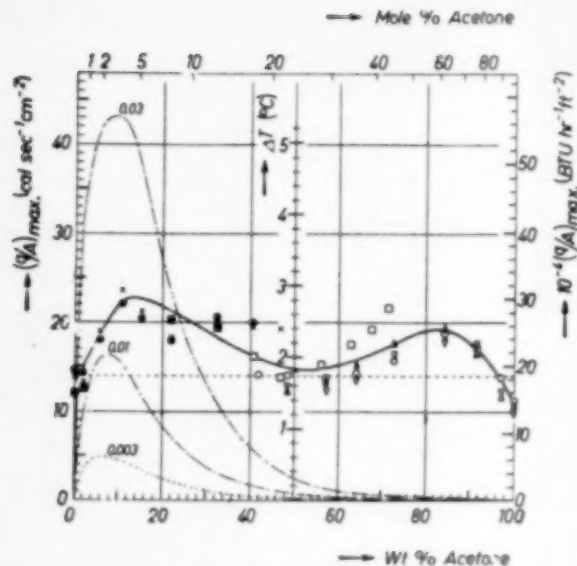


FIG. 5. Water—acetone. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

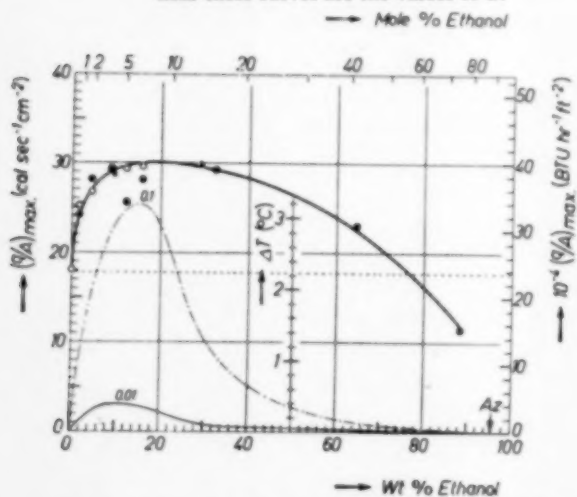


FIG. 6. Water—ethanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between the dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

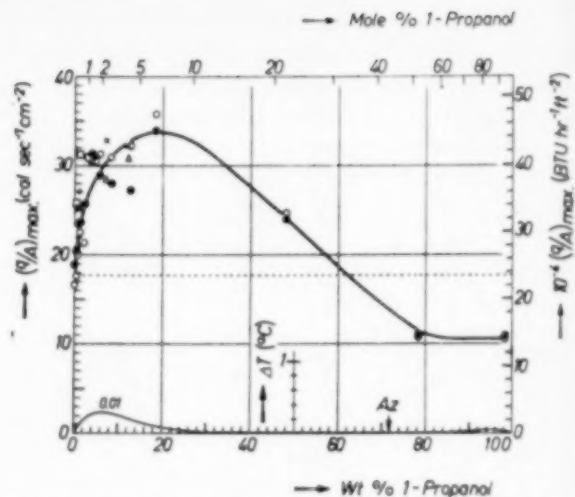


FIG. 7. Water—1-propanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope. The other curve represents ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The number near this curve is the value of G .

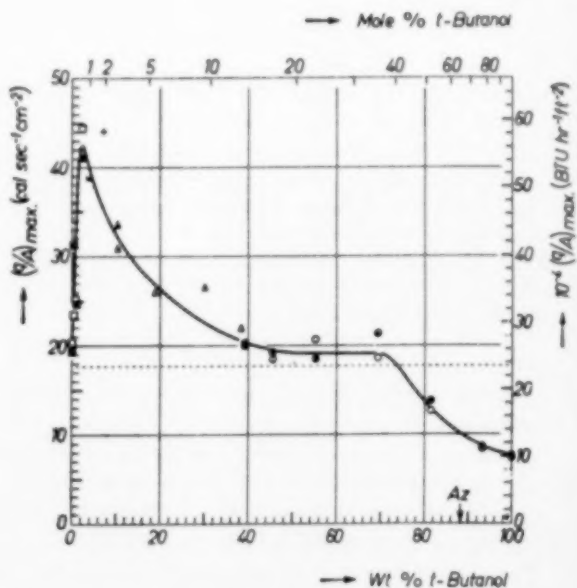


FIG. 8. Water—*t*-butanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope.

Mixtures of water with some lower aliphatic alcohols

Maximum heat flux for nucleate boiling was also determined as a function of concentration in mixtures of water—ethanol (Fig. 6), water—1-propanol (Fig. 7), water—t-butanol (Fig. 8), water—1-butanol (Fig. 9), water—1-pentanol (Fig. 10) and water—1-octanol (Fig. 11).

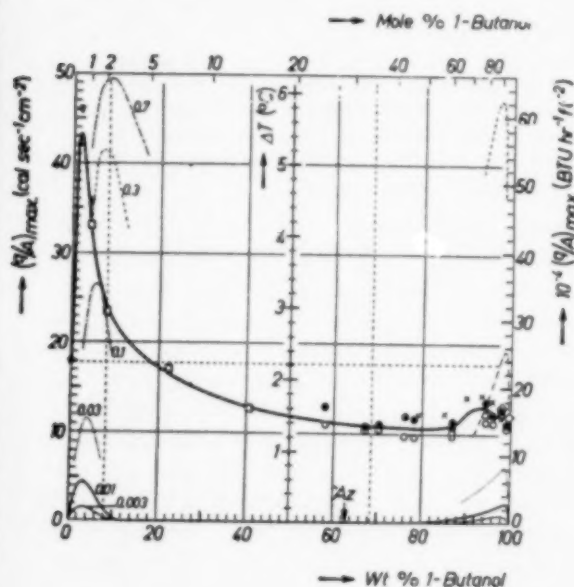


FIG. 9. Water-1-butanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope. The dotted vertical lines indicate the boundaries of the region of demixing at azeotropic boiling point. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

Increasing the number of carbon atoms in the alcohol series shifts the maximum towards lower alcohol concentrations. This maximum becomes higher and steeper from ethanol up to 1-pentanol, but it then decreases and for 1-octanol it is back again at the value of ethanol (compare Table 1).

With 1-pentanol the very high maximum value of $55 \text{ cal sec}^{-1} \text{ cm}^{-2}$ at 1.8% by weight pentanol is obtained at a boiling point of about 96°C . This is about $8\frac{1}{2}$ times as high as the maximum for water.

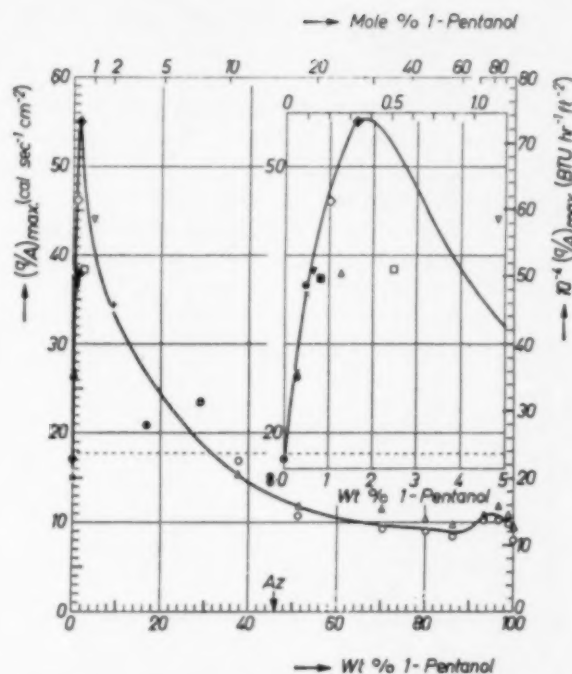


FIG. 10. Water-1-pentanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. Az = azeotrope.

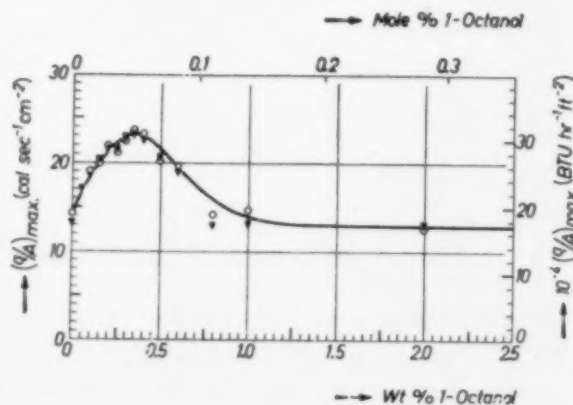


FIG. 11. Water-1-octanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures.

With 1-butanol and 1-pentanol a second maximum at high alcohol concentrations appears.

Again the curves do not show a discontinuity or a break if a second phase and emulsification

appear. This might be explained by assuming a preferential wetting of the heating surface by one of the phases.

It may be of importance to stress the fact that in all mixtures described in this paper no stable foaming was observed; however, at certain ranges of mixtures the size of the bubbles is definitely smaller, which causes more tendency to foaming.

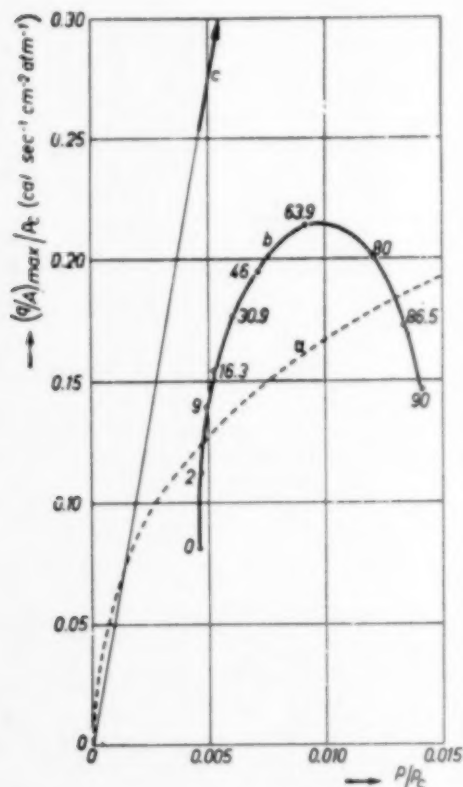


FIG. 12. Correlating maximum nucleate boiling heat flux. (a) Correlation by CICHELLI and BONILLA; (b) water—ethanol (the figures denote % by weight ethanol); (c) water—1-pentanol (1.8% by weight 1-pentanol).

With the data of critical pressures p_c for water—ethanol, determined by GRISWOLD [14] we plotted in Fig. 12 $(q/A)_{\max}/p_c$ as a function of reduced pressure $p_r = p/p_c$ in the same way as has been done by CICHELLI and BONILLA [7]. The dotted line (a) represents their correlation for several pure components and some mixtures at various pressures [4, 7]. This curve (a) shows a maximum at $p_r \approx 0.3$, which is not shown in Fig. 12.

The curve (b) — where the figures denote % by weight ethanol — represents our data for water—ethanol, and deviates from the curve (a) but shows essentially the same shape as the curve in Fig. 6; the maximum, however, is shifted now to a higher concentration.

For a 1.8% by weight mixture of 1-pentanol in water a $(q/A)_{\max}$ of $55 \text{ cal sec}^{-1} \text{ cm}^{-2}$ was observed. Although no critical pressures for this system are found in literature, an estimation of the situation of that mixture in Fig. 12 can be made, as it is reasonable to assume that the critical pressure for this mixture does not exceed that of water. This mixture namely shall be situated then on that part (c) of the straight line through the origin with a slope of $55 \text{ cal sec}^{-1} \text{ cm}^{-2} \text{ atm}^{-1}$, that is characterized by $p/p_c > 0.0045$ (the value for water). This means that for this mixture $(q/A)_{\max}/p_c$ might be at least twice as high as in the correlation.

In the mixtures discussed the most pronounced maximum was always found to occur for a concentration in which water was in excess. A qualitative explanation of this phenomenon is given below on the basis of the difference in volatility of the constituents in the mixture. On the strength of this theory a second maximum is expected to occur for a low water concentration, if water is considerably more volatile than the organic compound. The position of the second maximum for a low water concentration is in agreement with theory in case of 1-butanol and 1-pentanol.

If the mixture forms an azeotrope at a certain concentration, water is the more volatile component on one side of the azeotrope. If no azeotropic concentration exists, water is either the less volatile or the most volatile component throughout the entire range of concentrations. The latter situation is realized in mixtures of water and ethyleneglycol.

Mixtures of water—ethyleneglycol

In accordance with the theory only the second maximum heat flux when ethyleneglycol is in excess, is observed. This is shown in Fig. 18.

Mixtures of two organic components

Two binary systems (dioxane—methanol and 2-chloroethanol—di-iso-propylether) each consisting of organic compounds only, have been investigated to ascertain that the observed increased heat flux is not due to some property

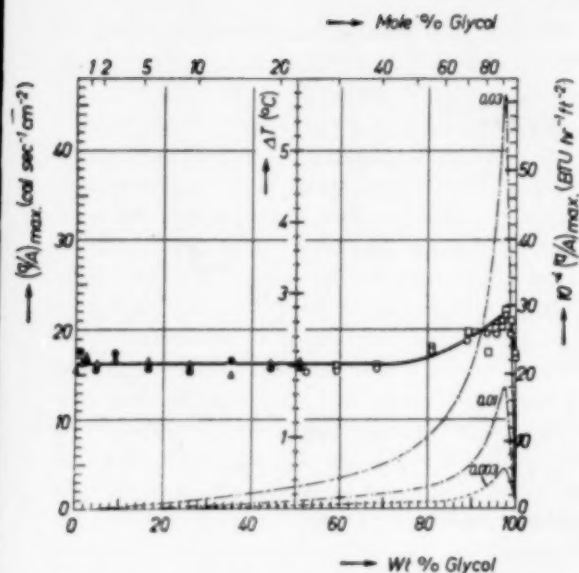


FIG. 13. Water—ethyleneglycol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

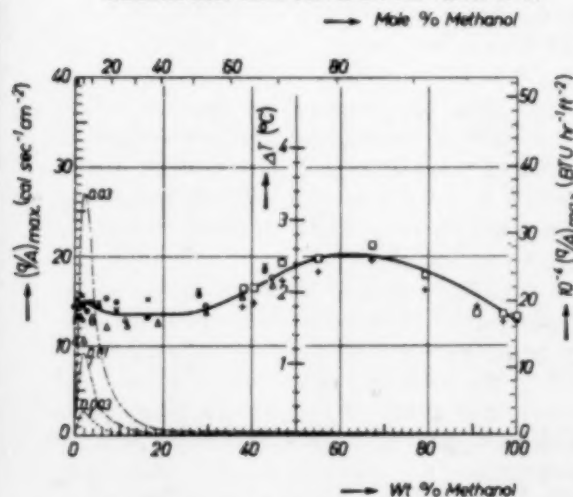


FIG. 14. Dioxane—methanol. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

characteristic for systems that contain water as a constituent. Here again qualitative agreement with theory is actually obtained. In Fig. 14 the curve for dioxane—methanol shows a little pronounced maximum at an excess concentration of dioxane. An additional maximum, however, appears—as was also the case in water—acetone mixtures—which cannot be explained by difference in volatility of the constituents in the mixture. The curve for 2-chloroethanol—di-iso-propylether in Fig. 15 shows a more pronounced maximum.

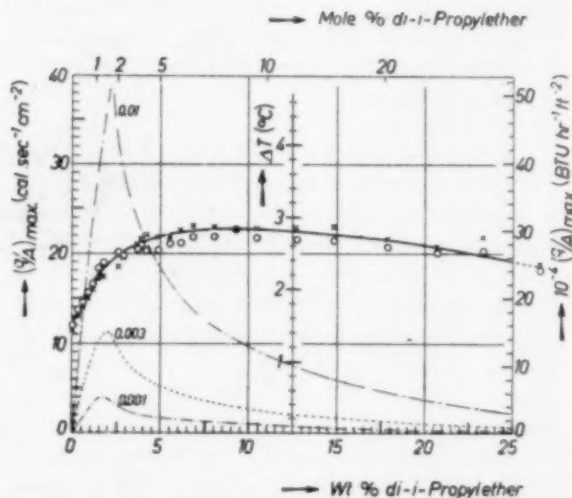


FIG. 15. 2-Chloroethanol—di-iso-propylether. Maximum heat flux q/A as a function of composition. Measurements carried out with the same wire are represented by the same figures. The other curves represent ΔT as a function of composition for a constant vaporized molar fraction G . ΔT is the difference between dew temperature of the vapour bubbles and boiling temperature of the original liquid. The numbers near these curves are the values of G .

QUALITATIVE EXPLANATION OF MAXIMUM HEAT TRANSFER

It has been shown by other investigators that most of the heat which is ultimately consumed in vaporization of water is first transferred to the bulk liquid in the neighbourhood of the heating surface, and only a small fraction is used for a direct formation of bubbles in contact with the heating surface [21]. The bulk liquid is slightly superheated and the small vapour bubbles

released from the heating surface grow rapidly during their passage through the liquid. Film-boiling starts if, owing to a larger temperature difference θ between heating surface and liquid, a vapour film is formed at the heating surface (Leidenfrost phenomenon), or if the vapour bubbles merge in the neighbourhood of the surface. Thus the smaller the average size of the bubbles leaving the heating surface, or the better the wetting, the more the onset of filmboiling is shifted towards higher heat flux.

If only one component is present, the vapour bubbles, which are assumed to be at their dew point, must always grow during passage through a superheated liquid; but this is no longer so in case of a mixture.

Let y and x be the molar fraction of the most volatile component in the binary mixture in the vapour phase and in the remaining liquid after vaporization respectively. Consider a system in which in a region of low concentrations, the organic component is more volatile than water. For equilibrium flash vaporization one has:

$$y = Kx \quad (1)$$

in which K is the equilibrium constant of the most volatile component. Let further x_0 be the molar fraction in the liquid phase before vaporization has taken place. Then, if a molar fraction G is vaporized, one has the relation:

$$(1 - G)x + Gy = x_0 \quad (2)$$

and from equations (1) and (2):

$$x = x_0 / 1 + (K - 1)G \text{ and } y = Kx_0 / 1 + (K - 1)G \quad (3)$$

The dew temperature of the vapour bubbles is equal to the boiling temperature of the remaining liquid and since x is smaller than x_0 (as $K > 1$) for the volatile component, the dew temperature of the bubbles $T + \Delta T$ exceeds the boiling temperature T of the original liquid. The dew temperature depends on the value of G . It can be calculated from equation (3). It is nearly equal to the boiling temperature of the original liquid if G is small and if $G = 1$ it is the temperature at which a vapour containing a molar fraction x_0 condenses.

Thus if the bubbles rise through a mass of superheated liquid of the original composition, it may happen that a certain value of G the dew temperature equals the temperature of the liquid.

One has then a situation in which the vapour in a bubble is in equilibrium with a liquid boundary layer which possesses a composition different from the surrounding liquid, but which has the same temperature as the latter. No heat flows from the superheated liquid to the boundary layer; and it is only owing to diffusional interchange between the boundary layer and the surrounding liquid that composition and dew temperature of the vapour will change and further vaporization can occur. A smaller size of bubbles resulting in a larger maximum heat transfer may then be expected.

Along this line of thought the occurrence of most of the maxima in the binary mixtures can be explained. In all cases investigated the size of the bubbles was actually a minimum at the maximum heat flux. As an example, the size of the bubbles is shown for water-1-butanol in the photographs of Fig. 16.

The dew temperature of the vapour minus the boiling temperature of the original liquid ΔT is plotted as a function of x_0 in Figs. 4, 5, 6, 7, 9, 18, 14 and 15. The value of G is constant on each curve. This dew temperature and the boiling temperature of the original liquid were read from graphs of the boiling temperature of the binary mixture as a function of x . The corresponding values of K were calculated from a curve giving y as a function of x .

A maximum value of ΔT occurs in all curves. In the case of the alcohols, these maxima occur at the same value of x_0 as the maximum heat flux if G is approximately 0.01. The difference ΔT is then some tenths of a degree centigrade. This is the same order of magnitude as found by other investigators for superheated pure water [22]. Since mixtures in the neighbourhood of the maximum heat flux consist mainly of water this is a satisfactory result. In mixtures of water-methyl-ethylketone a maximum value of ΔT as a function of concentration is found at a value of $x = 0.015$ (approximately 5% by weight). The position of this maximum is hardly dependent upon the

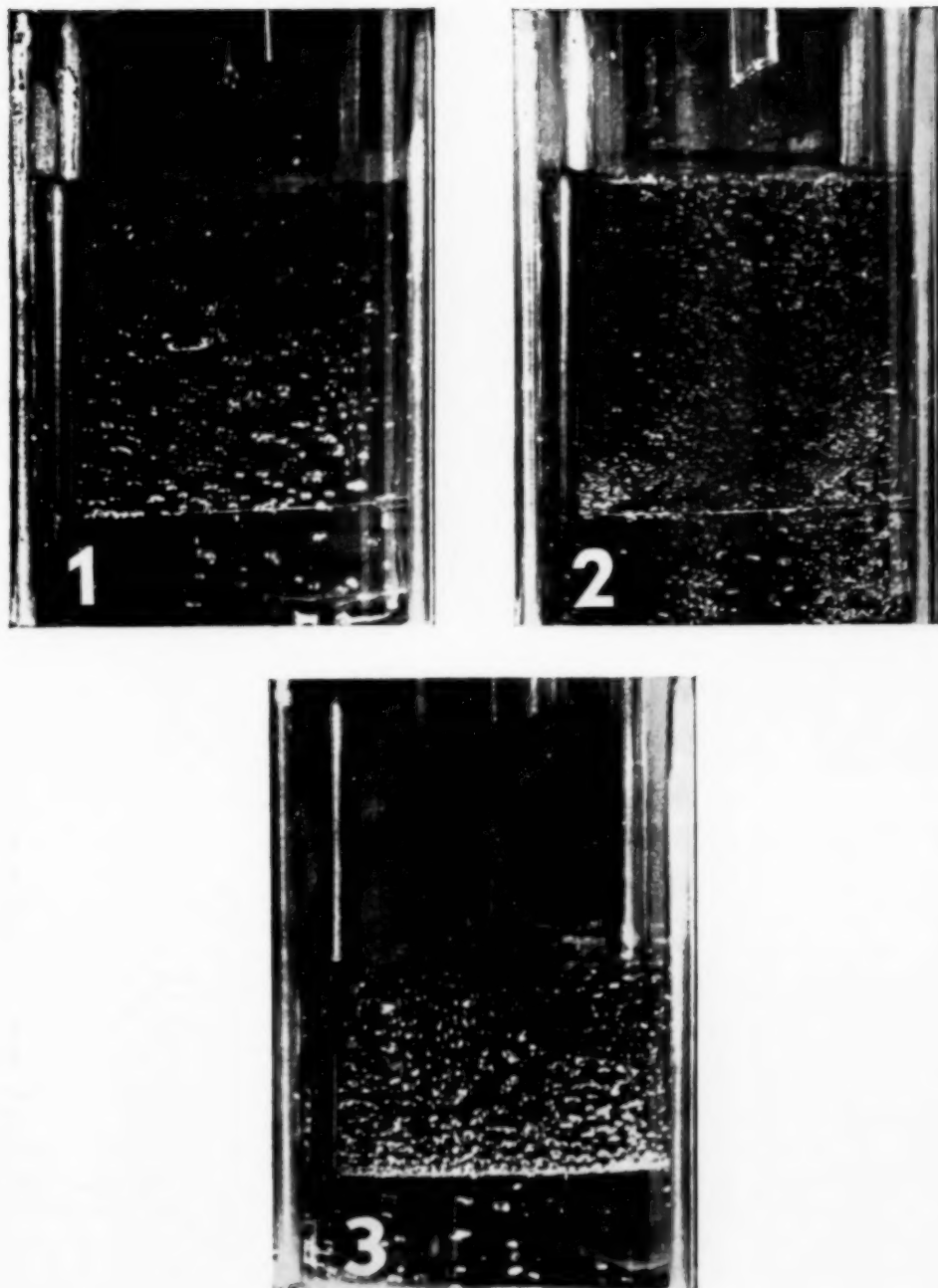


FIG. 16. *Water—1-butanol*. Photographs showing the size of vapour bubbles at constant heat flux ($7.5 \text{ cal sec}^{-1} \text{ cm}^{-2}$) for : 1. pure water, 2. water with 2% by weight 1-butanol, and 3. pure 1-butanol. The length of the heating wire is 6 cm and the diameter 0.02 cm.

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value of the vaporized fraction G . It is, therefore, impossible to select a value of G as the most probable one, by comparing the position of the maximum of the calculated value of ΔT with the actual position of maximum heat flux. If, however, ΔT maximum is assumed to be some tenths of a degree centigrade, a value of $G = 0.001$ is calculated. This is ten times smaller than in the case of the alcohols. For water—acetone $G = 0.003$ is determined and for the other systems investigated G cannot be estimated owing to lack of equilibrium data and information about the degree of superheating of organic liquids.

The value of G , however, will certainly depend upon the size of the bubbles which leave the heating surface [12, 13] and it may therefore be expected to depend upon the degree of wetting and the strength of adhesion of the liquid at the surface. If the organic component is enriched in a gas-liquid interface, and also in a solid-liquid interface in mixtures containing water as one component, as has been suggested by some authors [1, 2, 10, 30], a different original size of bubbles should be expected with different types of organic components. However, there are not at present, sufficient data available to permit a further discussion of this point.

It is found that all the maxima of maximum heat flux in nucleate boiling that are predicted by the theory are actually observed, although the second maximum occurring at a low concentration of water is much less pronounced than the first one. That the first maximum is lower with 1-octanol than with 1-pentanol, can be explained by the fact that in the former case the difference in boiling point between water and azeotrope is too small (see Table 1) to compensate the effect of superheating.

The conclusion seems to be justified that the position of maxima in maximum heat flux in binary systems can in general be predicted on account of equilibrium data only.

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NOTATION

A = Area of surface of test wire	cm^2
G = Vaporized molar fraction of liquid mixture	
$h = q/A\theta$ = Coefficient of heat transfer	$\text{cal sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$
h_{max} = Maximum nucleate boiling coefficient of heat transfer (at C in Fig. 1)	$\text{cal sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$
$K = y/x$ = Equilibrium constant of most volatile component in liquid mixture	
p, p_c and $p_r = p/p_c$ = Pressure, critical pressure and reduced pressure	atmosphere
q = Heat transfer rate	cal sec^{-1}
q/A = Heat flux	$\text{cal sec}^{-1} \text{cm}^{-2}$
$(q/A)_{\text{max}}$ = Maximum nucleate boiling heat flux (at C in Fig. 1)	$\text{cal sec}^{-1} \text{cm}^{-2}$
s, s_w, s_m = Solubility of component B in component A	$\text{g/100g, weight \% and mole \%}$
t = Temperature of surface of the test wire	$^\circ\text{C}$
T = Boiling point of liquid at atmospheric pressure	$^\circ\text{C}$
T_A, T_B, T_{Az} = Boiling point of component A, B and azeotrope	$^\circ\text{C}$
$\theta = t - T$ = Temperature difference between surface of wire and boiling liquid	$^\circ\text{C}$
ΔT = Temperature difference between dew point of vapour bubbles and boiling point of original liquid	$^\circ\text{C}$
x = Molar fraction of most volatile component in liquid	
x_0 = Original molar fraction of most volatile component in liquid (before vaporization takes place)	
y = Molar fraction of most volatile component in vapour	

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Optimum temperature gradients in tubular reactors—I

General theory and methods

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Abstract—In this paper the mathematical techniques necessary for the determination of the optimum temperatures profile in a tubular reactor to insure maximum yields or minimum contact times are developed, and applications are made to reversible and consecutive reaction systems. The problem is shown to be reducible to a system of ordinary non-linear differential equations. The solution of these differential equations can be made by conventional numerical methods, and will allow the specification of the temperatures in the reactor. In a succeeding paper numerical calculations obtained with an analogue computer (REAC) will be presented. The problem of two consecutive reactions $A \rightarrow B \rightarrow C$, in which the reactions are of first or second order, is discussed in detail. The method of attack on more complicated problems is sketched. It is shown in general that appreciable gains in the yield may be obtained if the optimum temperature distribution is used.

Résumé—On a développé ci-dessous les méthodes mathématiques qui permettent de déterminer, pour un réacteur tubulaire, le profil de température donnant la production maximum ou le temps de contact minimum pour une production donnée. Ces méthodes sont appliquées à des systèmes de réactions réversibles ou consécutives.

On montre que le problème se réduit à la résolution d'un système d'équations différentielles non-linéaires. Ce système se résout par les méthodes numériques usuelles et permet de spécifier les températures optima le long du réacteur. Le problème de deux réactions consécutives $A \rightarrow B \rightarrow C$ dans lequel les réactions sont soit du premier soit du second ordre est étudié en détail et les méthodes à employer pour résoudre des cas plus compliqués sont décrites. En général, des gains appréciables sur la production pourraient être théoriquement obtenus en utilisant la distribution de température optimum.

Une publication future donnera des exemples numériques résolus à l'aide d'un calculateur analogique (REAC).

1. INTRODUCTION

Successful reactor design is dependent upon the proper choice of several operating variables, namely pressure, temperature, and concentrations. Pressure, or what may sometimes be equivalent, the proportion of inerts in the feed, may be varied to change reaction rates or displace equilibria. An example of the proper choice of concentrations is afforded in those processes in which an unwanted product given by a reversible reaction is recycled. If its concentration is maintained at the equilibrium value, no new waste product will be formed.

Because of the sensitivity of many reactions to temperature, the control of temperature may be very important. For a single irreversible reaction the optimum temperature will usually be chosen as the highest temperature compatible with the materials of construction, the properties of the catalyst, the problem of preheating to high temperatures without decomposition, and the problems of heat transfer which arise at high reaction rates. In some cases, however, when the reaction is surface catalysed, an increase in the temperature above a certain limit precipitates gas desorption, and this factor may well offset

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the increase in the reaction rates. Thus the problem of optimum temperature deserves careful study.

The purpose of this paper is to analyse the problem of the optimum temperature in a tubular reactor. For single reactions this calculation may be simple. In many cases of industrial importance, however, the desired product results from a process which involves consecutive or competing reactions. The usual design procedure in this case is to choose operating conditions at which the unwanted reactions have negligible rates. This is not always possible, and a temperature variation along the axis of the reactor may prove useful in increasing the yield. This may require elaborate heat transfer equipment and control instrumentation along the reactor, or the use of a series of adiabatic reactors and intercoolers. The calculation of the optimum ideal temperature profile is a serious problem when the kinetic scheme involves consecutive or competing reactions and no published solution is known.

The definition of what one means by an optimum operation depends upon the economics of the process, the main factors of which are the process time and the process yield. Many approaches to the problem are possible. One might ask, for example, what the best temperature for isothermal operation is, if any. This will be referred to in the future as the optimum isothermal temperature. Secondly, one might ask for the optimum yield in a fixed process time or reactor volume. This is clearly the case in which capital investment would be a controlling factor, since process time or reactor volume determines equipment size and construction costs directly. Thus a balance between installation costs and output value will then determine the optimum process time. In a sense this is a minimax problem since the yield is a maximum for each process time but the process time is fixed to minimize the total cost (or maximize the profit). Another approach to this same problem is possible. One can determine the temperature profile along the reactor which will produce a given yield of the desired substance in minimum process time, and determine this minimum process time as a function of the yield. It is a remarkable fact that the

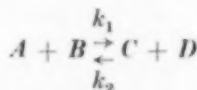
solution to both of these problems is intrinsically the same, and leads to the same temperature profile.

These problems will be discussed in this and the following paper. It is apparent that such problems will lead to complex mathematical analyses. The equations which arise were solved on the REAC, an electronic analogue computer manufactured by the *Reeves Company*. Since the purpose of this paper is, largely, to illustrate the mathematical methods and techniques, the physical model assumed will be a very simple one. Complicating features will be omitted, but it is hoped that enough of the problem has been included so that the whole is not meaningless.

This paper should be considered as an exploratory one in which the mathematical methods and numerical techniques are presented.

2. SIMPLE REACTIONS*

Simple reactions are those in which a single reversible reaction determines the rate of the process. Examples of these are the ammonia synthesis and sulphur dioxide oxidation. Suppose the reaction



is reversible, second order in each direction, exothermic, and is carried out in a tubular reactor. In this case the equilibrium constant decreases as the temperature increases, and it is clear that a high yield at the reactor outlet demands a low temperature. On the other hand, at the reactor inlet equilibrium considerations are not important, and the temperature may be very high in order to increase the rate of the reaction. Thus on this simple example it appears that a falling temperature gradient is necessary to produce a high yield in a short time. It is obvious, of course, that if the total contact time is immaterial the temperature should be chosen at a low level in order to give a high yield.

* The authors are indebted to K. G. DENBIGH, who introduced them to these problems while he was a Visiting Professor in the Chemical Engineering Department at the University of Minnesota in 1953-54.

If G is the total mass flowing through the reactor, x is the reactor length, C_A the concentration of A in moles per unit mass of reaction mixture, a the initial value of C_A , and p the total pressure, M the molecular weight, and T the temperature, then the kinetic expression for the reactor is

$$-G \frac{dC_A}{dx} = \left(\frac{pM}{RT}\right)^2 [k_1 C_A^2 - k_2 (a - C_A)^2] \quad (1)$$

Integration at constant T and p gives, $K = \frac{k_1}{k_2}$,

$$F = x \left(\frac{pM}{R}\right)^2 \frac{2a}{G} = \frac{\sqrt{KT^3}}{k_1} \log_e \left[\frac{C_A(\sqrt{K}-1)+a}{C_A(\sqrt{K}+1)-a} \right] \quad (2)$$

In order best to illustrate how the function F depends upon the temperature a simple numerical case will be considered. If one chooses the numerical values

$$C_A = 0.80 a \text{ at the outlet}$$

$$C_A = a = C_B \text{ at the inlet, } c = 0 = d$$

$$p = 1 \text{ atm.}$$

$$\text{Mol.wgt. } A = 46, \text{ Mol.wgt. } B = 54, M = 50$$

$$p_1 = 4.85 \times 10^{13}, E_1 = 25,000$$

$$p_2 = 7.42 \times 10^{14}, E_2 = 30,000$$

$$K = 5.86 \times 10^{-2} \exp \left(+ \frac{5000}{RT} \right), -\Delta H = 5,000$$

then the function F may be plotted as a function of the temperature. This has been done in Fig. 1, and a minimum in the curve results. Thus, to design a reactor for minimum volume, one must operate at 550°K, and note that the minimum is a sharp one. It is also interesting that the optimum isothermal temperature, optimum in the sense of fixed conversion in minimum time, occurs within 5°K of the outlet equilibrium temperature.

Equation (1) may be written in two forms

$$dx = G \left(\frac{RT}{pM}\right)^2 \frac{-dC_A}{k_1 C_A^2 - k_2 (a - C_A)^2} \quad (3)$$

$$dC_A = - \left(\frac{pM}{RT}\right)^2 \frac{1}{G} [k_1 C_A^2 - k_2 (a - C_A)^2] dx \quad (4)$$

The first may be integrated to give

$$F = \frac{2ax}{G} \left(\frac{pM}{R}\right)^2 = 2a \int_a^{C_A} \frac{-T^2 dC_A}{k_1 C_A^2 - k_2 (a - C_A)^2} \quad (5)$$

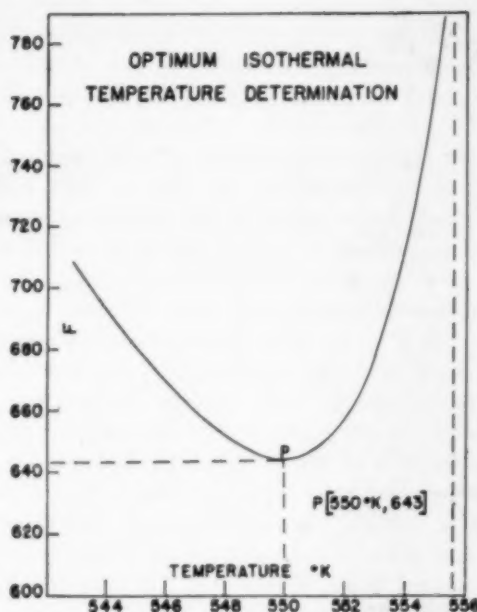


FIG. 1. Determination of the optimum isothermal temperature for a reaction of the type $A + B \rightleftharpoons C + D$, exothermal and second order in each direction.

In equation (5) the value of F , and hence x , depends upon how the temperature variation along the reactor is chosen. If one specifies how T depends upon x or C_A then from equations (3) and (4) one may compute how C_A depends upon x , and the integral in equation (5) may be evaluated. The value of this integral thus depends on the temperature variation along the reactor, and it is interesting to ask what temperature variation will make the value of this integral the least possible. This is an elementary problem in the calculus of variations, and Euler's equation is the necessary condition that the integral have an extremal, which is in this case

$$\frac{\partial}{\partial T} \left[\frac{k_1 C_A^2 - (a - C_A)^2 k_2}{T^2} \right] = 0 \quad (6)$$

or

$$\frac{k_1 E_1 - 2RT}{k_2 E_2 - 2RT} = \frac{(a - C_A)^2}{C_A^2} \quad (7)$$

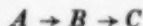
In section 6 it will be shown that the problem of calculating the maximum yield in a fixed time has the same answer, i.e. the optimum gradients necessary in each case are the same.

Equation (7) determines the temperature if the concentration is known and hence the temperature is fixed locally and does not depend upon the history of the system. Equation (6) says, in effect, that the reaction rate is to be maximized with respect to the temperature at each point. The temperature variation along the reactor may then be computed using equation (7) and a step by step procedure using equation (8). From equation (7) at the entrance of the reactor, $C_A = a$, $T = E_1/2R$. This temperature is much too high in general for practical operation, and some arbitrarily fixed upper temperature is chosen. If one chooses, for example, this upper temperature at 870°K, operating isothermally at this temperature until the concentration and 870°K satisfy equation (7), and follows this section of the reactor with a temperature gradient calculated from equation (7), it is found that $F = 305$. For the isothermal case $F = 643$, and therefore the reactor volume is halved if the optimum gradient is used. It should be pointed out, however, that heat removal requirements have not been considered, and could be so severe as to make the optimum gradient impossible of attainment.

Problems similar in nature to this one have been treated by DENBIGH [4], ANNABLE [1], CALDERBANK [8], and TEMKIN and PYZHEV [7].

8. THEORY FOR TWO CONSECUTIVE REACTIONS

Consider the system of two consecutive reactions



The feed is component A , and B is the product of interest, the yield of which is to be maximized. Component C is a waste product.

If one supposes that the activation energy of the second reaction is greater than that of the first, then a high temperature will produce more C than desired. It is therefore apparent that, near the end of the reaction time when the concentration of B is high, the temperature must be low. On the other hand, at the beginning of the reaction when the concentration of B is low the temperature may be high, since there is little B in the system and hence little C can be formed. It

seems intuitive therefore that if $E_2 > E_1$ there should be a falling temperature gradient along the axis of the reactor.

The method of attack will be demonstrated on the simple case in which both reactions are of the first order. The technique will then be extended to a more general case, more interesting practically. The letters x and y in the future will be concentrations and t will be the time. Since pressure changes are to be neglected, the equations for the tubular reactor have essentially the same form as those for the batch reactor. Assume then that the kinetics of the system are described by

$$\frac{dx}{dt} = -a(T)x \quad (8)$$

$$\frac{dy}{dt} = a(T)x - b(T)y \quad (9)$$

where $a(T)$ and $b(T)$ are the specific rate constants. Our aim is to determine the temperature $T(t)$ and therefore the temperature profile in the reactor which will give the maximum value to the yield y at a given reaction time t equal to θ . In the course of the problem $a(t)$ and $b(t)$ will be the specific rate constants obtained by replacing T by the appropriate function of the time. The solution to the set of equations (8) and (9) is given by

$$x(t) = x_0 e^{-\int_0^t a(\beta) d\beta} \quad (10)$$

$$y(t) = y_0 e^{-\int_0^t b(\beta) d\beta} + x_0 \int_0^t a(\beta) e^{-\int_0^\beta a(\gamma) d\gamma} e^{-\int_\beta^t b(\gamma) d\gamma} d\beta \quad (11)$$

where x_0 and y_0 are the feed concentrations of A and B . The expressions $x(t)$ and $y(t)$ describe the composition of that part of the reacting mixture which entered the reactor at time zero.

At every instant t during the course of the process, the part of the reacting mixture under observation assumes a temperature T . Thus let T_i be the temperature at the instant t_i , with $0 < t_i < \theta$. The yield of y thus depends on an

infinity of variables, the temperature T_i at the instants t_i during the course of the process. The function y may then be considered as a function of the independent variables T_i . If one supposed that the reactor were divided up into a finite number of sections, each section having a temperature T_i , then equation (11) could be written as a sum of terms, each term describing a certain isothermal section of the reactor. The yield y at the reactor outlet would then be a function of all these temperatures and the condition for an extremal would be

$$\frac{\partial y(\theta, T_i)}{\partial T_i} = 0 \quad \text{for all } i \quad (12)$$

However, here the variables T_i are not discrete but form an infinite set defined on the time interval $(0, \theta)$. The dependence of y on T is then described mathematically by saying that y is a functional of the temperature, a functional being a quantity which depends on the entire course of one or more functions rather than on a number of discrete variables. The notation

$$y(\theta, [T])$$

will be used to denote this functional dependence of the yield on the temperature.

Consider a function $T_0(t)$ which gives rise to a yield $y_0 = y(\theta, [T_0(t)])$ and a function $T_1(t)$ which is equal to $T_0(t)$ everywhere outside an interval $t_a < t < t_b$. In this interval

$$T_1(t) = T_0(t) + \delta T(t)$$

The yield with the temperature $T_1(t)$ is $y_1 = y(\theta, [T_1(t)])$ and the average variation in y due to the disturbance $T(t)$ around $t = t_i$ is given by

$$\begin{aligned} \Delta y(\theta, [T]) &= \frac{1}{\Delta t} \int_{t_a}^{t_b} [y(\theta, [T_1(t)]) - y(\theta, [T_0(t)])] dt \\ &= \frac{1}{\Delta t} \int_{t_a}^{t_b} \frac{\partial y(\theta, [T(t)])}{\partial T_{t=t_i}} \delta T(t) dt + O\left(\int_{t_a}^{t_b} [\delta T(t)]^2 dt\right) \end{aligned}$$

with $\Delta t = t_b - t_a$, after a development in Taylor series of the functional y . This may be written

$$\Delta y(\theta, [T]) = \frac{1}{\Delta t} \frac{\partial y(\theta, [T(t)])}{\partial T_{t=t_i}} \int_{t_a}^{t_b} \delta T(t) dt$$

where $t_a < t_i < t_b$. As $t_a \rightarrow t_i$ and $t_b \rightarrow t_i$, then the point variation of the functional y may be defined as

$$\delta y(\theta, [T])_{at t_i} = \lim_{\substack{t_a \rightarrow t_i \\ t_b \rightarrow t_i}} \frac{\Delta y(\theta, [T])}{t_b - t_a}$$

Calling

$$\delta T_1 = \lim_{t_a \rightarrow t_b} \frac{1}{t_b - t_a} \int_{t_a}^{t_b} \delta T(t) dt$$

then

$$\delta y(\theta, [T])_{at t_i} = \frac{\partial y(\theta, [T])}{\partial T_{t=t_i}} \delta T_i$$

The derivative

$$\frac{\partial y(\theta, [T])}{\partial T_{t=t_i}} \quad (18)$$

expresses the dependence of the yield on the temperature encountered by the reacting mixture at a time $t = t_i$. Such expressions are called partial functional derivatives. They have been introduced mostly by VOLTERRA [8] and a good account of functional analysis may be found in LEVY [5, 6]. Hence the extremal condition will be expressed by setting the partial functional derivative of the yield with respect to the temperature equal to zero for all values of t_i in $(0, \theta)$. This condition, which is essentially equation (12) extended for functionals, will then determine the values of the variables T_i , that is to say the function $T(t)$, which describes the optimum temperature profile in the reactor.

In calculating the quantity given in equation (18) it is simpler, intuitively, if one thinks of the T_i 's as being discrete variables. In equation (11), β varies from 0 to θ and ultimately passes the point t_i at which the variable T_i enters into play. The partial functional derivative will therefore have different contributions arising from the different portions of the time interval $(0, \theta)$,

$$0 < \beta < t_i$$

$$\beta = t_i$$

$$t_i < \beta < \theta$$

Carrying out this operation, there results

$$\begin{aligned} \frac{\partial y(\theta, [T])}{\partial T_i} = & -b_T'(T_i) y_0 e^{-\int_0^\theta b(T) d\beta} \\ & -b_T'(T_i) x_0 \int_0^{t_i} a(T) e^{-\int_0^\beta a(T) d\gamma - \int_\beta^\theta b(T) d\gamma} d\beta \\ & + a_T'(T_i) x_0 e^{-\int_0^{t_i} a(T) d\gamma - \int_{t_i}^\theta b(T) d\gamma} \\ & -a_T'(T_i) x_0 \int_{t_i}^\theta a(T) e^{-\int_0^\beta a(T) d\gamma - \int_\beta^\theta b(T) d\gamma} d\beta \end{aligned}$$

The extremal condition, obtained by setting this equal to zero for all i , becomes

$$a_T'(T_i) x(t_i) - b_T'(T_i) y(t_i) = x_0 a_T'(T_i) \int_0^{t_i} a(T) e^{-\int_0^\beta a(T) d\gamma - \int_\beta^{t_i} b(T) d\gamma} d\beta$$

As this expression must be valid for all values of t_i between 0 and θ , one may replace t_i by t . Replacing also T by its unknown expression as a function of the time, and setting

$$\frac{b_T'(T)}{a_T'(T)} = A(T) \quad (18)$$

one finally obtains

$$x(t) - A(t)y(t) = x_0 \int_0^t a(\beta) e^{-\int_0^\beta a(\gamma) d\gamma - \int_\beta^t b(\gamma) d\gamma} d\beta \quad (14)$$

In order to obtain a more manageable expression equation (14) may be differentiated with respect to the time to give

$$A_T'(T) \frac{dT}{dt} = [b(T) - a(T) A(T)] \frac{x}{y} \quad (15)$$

Equation (15), when combined with a suitable auxiliary condition, is completely equivalent to equation (14).

Thus the solution of the system of simultaneous differential equations (8), (9) and (15), gives the

solutions $x(t)$, $y(t)$, and $T(t)$ dependent on the initial values x_0 , y_0 and T_0 which are related to θ by equation (14) and which may be put in the form

$$x_0 + [1 - A(T_0)] y_0 = y(\theta) e^{\int_0^\theta b(x_0, y_0, T_0, \gamma) d\gamma} \quad (16)$$

If x_0 and y_0 are given, equation (16) determines the relation between the process time θ and the optimum initial temperature T_0 . Formally then our problem is solved through the system

$$\frac{dx}{dt} = -a(T)x \quad (8)$$

$$\frac{dy}{dt} = a(T)x - b(T)y \quad (9)$$

$$\frac{dT}{dt} = \frac{b(T) - a(T) A(T) x}{A_T'(T) y} \quad (15)$$

The kinetic constants $a(T)$ and $b(T)$ are usually of the Arrhenius form and the above equations are non-linear but may be solved numerically by well-known methods. Such a numerical solution may be performed if the initial values x_0 , y_0 , and T_0 are given. However, the quantities usually given will be x_0 , y_0 and θ . In this case one must assume an initial value for the temperature, T_0 . The differential equations may then be solved. The time for which this solution satisfies the extremum conditions is given by equation (14), for when $t = \theta$,

$$x(\theta) - A(\theta)y(\theta) = 0.$$

For convenience

$$Z(t) = x(t) - A(t)y(t) \quad (17)$$

or similar functions which will be encountered later, will be called the "zero function." $Z(t)$ has the property of being equal to zero at $t = \theta$, and θ is thus easily determined by following the behaviour of $Z(t)$ during the course of a numerical solution starting with an assumed value of T_0 . The temperature profile itself will be obtained by eliminating x and y from equations (8), (9), and (15) to give

$$\frac{d^2 T}{dt^2} + \frac{a(T) - B_T'(T)}{B(T)} \left(\frac{dT}{dt} \right)^2 + [a(T) - b(T)] \frac{dT}{dt} = 0 \quad (18)$$

where

$$B(T) = \frac{b(T) - a(T) A(T)}{A_T'(T)} \quad (18')$$

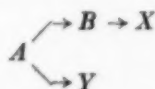
The initial conditions to be associated with equation (18) are T_0 and $\left(\frac{dT}{dt} \right)_0$, and are related to x_0 , y_0 , and θ through equation (16) and equation (15)

$$\left(\frac{dT}{dt} \right)_0 = B(T_0) \frac{x_0}{y_0}$$

This last relation shows that if there is no trace of component B in the feed, the optimum solution calls for an infinite temperature gradient at the reactor entrance. It should also be remarked that rather large deviations from the theoretical optimum temperature profile should have a small effect on the optimum yield of B because of the stationary nature of the optimum profile. This effect is counterbalanced by the sensitivity of the rate constants to temperature.

4. A MORE COMPLICATED CASE

To illustrate further the method of derivation of the equation defining the optimum temperature profile, a more complicated case involving both consecutive and side reactions will be treated. Consider the kinetic scheme



Feed component A gives the product of interest B by a second order reaction. Product B decays to waste X by a first order process. At the same time a competitive reaction occurs; feed component A is destroyed by a first order process and gives a waste product Y . It is desired to maximize the yield of B . In this model the kinetic scheme is

$$\frac{dx}{dt} = -a(T)x^2 - c(T)x \quad (19)$$

$$\frac{dy}{dt} = a(T)x^2 - b(T)y \quad (20)$$

where a , b , c are the specific rate constants of the respective reactions $A \rightarrow B$, $B \rightarrow X$, $A \rightarrow Y$ or appropriate modifications if volume changes during the course of the reaction are serious. Equations (19) and (20) may be solved in closed form to give

$$x(t) = x_0 H(t) \quad (21)$$

$$y(t) = y_0 e^{-\int_0^t b(\gamma) d\gamma} + x_0 \int_0^t x_0 a(\beta) \overline{H(\beta)}^2 e^{-\int_0^t b(\gamma) d\gamma} d\beta \quad (22)$$

where $H(t)$ is defined by

$$\overline{H(t)}^{-1} = 1 + x_0 \int_0^t a(\beta) e^{-\int_0^\beta c(\gamma) d\gamma} d\beta.$$

As in the preceding case the temperature has been replaced by its expression as a function of reaction time in the kinetic rate constants.

The partial functional derivative of the yield of B with respect to the temperature at a given time t will be evaluated. The process is carried out as before, the intervals $(0, t)$ and (t, θ) giving different contributions to the derivative. However, the different functionals of temperature which enter into the expression of the yield are more complex and the example provides a good illustration of the application of the method to more difficult cases. Thus

$$\begin{aligned} \frac{\partial y(\theta, [T])}{\partial T} = & -2 \int_0^t x_0^2 a(\beta) \overline{H(\beta)}^3 \left[c_T'(t) \int_0^t a(\gamma) e^{-\int_0^\gamma c(\rho) d\rho} d\gamma \right. \\ & \left. + a_T'(t) e^{-\int_0^t c(\rho) d\rho} \right] \cdot e^{-\int_0^t b(\gamma) d\gamma} d\beta \\ & - b_T'(t) \int_0^t x_0^2 a(\beta) \overline{H(\beta)}^3 e^{-\int_0^t b(\gamma) d\gamma} d\beta \end{aligned}$$

$$- b_T'(t) y_0 e^{-\int_0^t b(\gamma) d\gamma} \\ + x_0^2 a_T'(t) \overline{H(t)}^2 e^{-\int_0^t b(\gamma) d\gamma}$$

After substitutions from equations (21) and (22) and elimination of the common factor

$$e^{-\int_0^t b(\gamma) d\gamma}$$

the cumbersome expressions above give the following equation, which expresses the vanishing of the partial functional derivative of y ,

$$a_T'(t) x^2(t) - b_T'(t) y = \left[c_T'(t) \left(\frac{1}{x} - \frac{1}{x_0} \right) + a_T'(t) \right] \int_0^t 2a(\beta) \overline{x(\beta)}^2 e^{-\int_0^t [b(\gamma) + c(\gamma)] d\gamma} d\beta \quad (23)$$

Equation (23) is the analogue of equation (14). The differential equation for the temperature gradient may be obtained as before

$$\frac{dT}{dt} = \frac{(x^2 - Ay) \frac{C}{x} (ax + c) - \left[1 + C \left(\frac{1}{x} - \frac{1}{x_0} \right) \right] P}{[(AC_T' - CA_T')y - x^2 C_T'] \left(\frac{1}{x} - \frac{1}{x_0} \right) - y A_T'} \quad (24)$$

with

$$P = \left[(b - aA)x^2 - cAy + 2aCx^2 \left(\frac{1}{x} - \frac{1}{x_0} \right) \right]$$

where

$$C(T) = \frac{c_T'(T)}{a_T'(T)} \\ A(T) = \frac{b_T'(T)}{a_T'(T)}$$

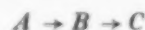
It would be possible to eliminate the concentrations x and y of components A and B among equations (19), (20), and (24) in analogy with what was done in the previous example, but

the complexity of the expressions thus obtained makes this procedure lose its interest in the present case.

A remark in taking the partial functional derivative may be worth making. If one thinks of the integrals appearing in the expression for the yield of B as sums, infinite to be sure, then the derivative may be taken in the standard way, and affects only those terms of the sum which depend on the value i of the index. Once the derivative has been taken the sums then revert to integrals. This is certainly not rigorous but it is a convenient way of thinking about the problem.

5. THE IMPLICIT METHOD

The method explained above is dependent upon the existence of closed solutions of the kinetic equations of the system. It is a fact, however, that even in rather simple cases - for instance a first order reaction followed by a second order one - these closed solutions are not known or, if known, are unwieldy. This does not prevent the solution of the kinetic equations by numerical methods. It seemed interesting, therefore, to devise a method of obtaining the equation which defines the optimum temperature profile, which would not make use of closed solutions. Consider again a system of two consecutive reactions



where B is the component of interest and assume that the kinetics are now represented by the more general form

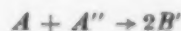
$$\frac{dx}{dt} = -a(T)F(x) \quad (25)$$

$$\frac{dy}{dt} = na(T)F(x) - b(T)G(y) \quad (26)$$

Thus, this representation may include reactions of the form



or



The letters x and y designate the concentrations of components A and B . $a(T)$ and $b(T)$ are the kinetic rate constants of the two consecutive reactions, and $F(x)$ and $G(y)$ depend on the order and assume mechanism of the reactions but do not contain the temperature variable. The coefficient n has been introduced to include cases of the form $A \rightarrow 2B \rightarrow C$ where there is a change in stoichiometric coefficients or cases like the second example above, where a parallel reaction of essentially the same mechanism competes with the reaction giving component B .

Consider then the partial functional derivations

$$\frac{\partial x(t, [T])}{\partial T_i} \quad \text{and} \quad \frac{\partial y(t, [T])}{\partial T_i}$$

the index i on T being dropped whenever there is no danger of confusion. The T_i 's are independent variables and are not functions of the time t . Thus the order of the differentiations with respect to T_i and t may be changed without affecting the derivative thus obtained. Therefore, one may write, using equations (25) and (26)

$$\begin{aligned} \frac{d}{dt} \left(\frac{\partial x}{\partial T_i} \right) + a(T) F'(x) \frac{\partial x}{\partial T_i} \\ = -\delta(t - t_i) a_T'(T) F(x) \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{d}{dt} \left(\frac{\partial y}{\partial T_i} \right) + b(T) G'(y) \frac{\partial y}{\partial T_i} \\ = \delta(t - t_i) [na_T'(T) F(x) - b_T'(T) G(y)] \\ + na(T) F'(x) \frac{\partial x}{\partial T_i} \end{aligned} \quad (28)$$

The symbol $\delta(t - t_i)$ is the Dirac delta function, and no rigorous mathematical significance should be attached to its use. It should rather be understood as a convenient symbolism, the proper use of which allows us to bypass a rigorous but cumbersome derivation of the result. $\delta(t - t_i)$ is equal to zero for $t \neq t_i$, and is infinite at $t = t_i$ such that

$$\int_{t_i - \epsilon}^{t_i + \epsilon} \delta(t - t_i) dt = 1$$

Taking into consideration the fact that for $t < t_i$

$$\frac{\partial x}{\partial T_i} = 0 \quad \text{and} \quad \frac{\partial y}{\partial T_i} = 0$$

Equations (27) and (28) may be solved. Equation (27) is an ordinary differential equation in $\frac{dx}{dT_i}$ whose solution is

$$\frac{\partial x}{\partial T_i} = - \int_0^t \delta(\beta - t_i) a_T'(\beta) F(x) e^{\int_0^\beta a(\gamma) F'(x) d\gamma} d\beta$$

and hence (since $\delta(\beta - t_i)$ is a kernel function for a singular integral)

$$\frac{\partial x}{\partial T_i} = -a_T'(T_i) F(x_i) e^{-\int_{t_i}^t a(\gamma) F'(x) d\gamma}$$

where T_i and x_i are the values of the temperature and the concentration of A at time t_i . Equation (28) may then be written in the form

$$\begin{aligned} \frac{d}{dt} \frac{\partial y}{\partial T_i} + b(T) G'(y) \frac{\partial y}{\partial T_i} \\ = \delta(t - t_i) [na_T'(T) F(x) - b_T'(T) G(y)] \\ - na(T) F'(x) a_T'(T) F(x_i) e^{-\int_{t_i}^t a(\gamma) F'(x) d\gamma} \end{aligned}$$

Then

$$\begin{aligned} \frac{\partial y}{\partial T_i} = \int_0^t \delta(\beta - t_i) [na_T'(T) F(x) \\ - b_T'(T) G(y)] e^{\int_0^\beta b(\gamma) G'(y) d\gamma} d\beta \\ - \int_{t_i}^t na(T) F'(x) a_T'(T_i) \\ \cdot e^{-\int_{t_i}^\beta a(\gamma) F'(x) d\gamma + \int_0^\beta b(\gamma) G'(y) d\gamma} F(x_i) e d\beta \end{aligned}$$

or

$$\begin{aligned} \frac{\partial y}{\partial T_i} = & \left[n a_T'(T_i) F(x_i) \int_{t_i}^{t_i} b(\gamma) G'(y) d\gamma \right. \\ & \left. - b_T'(T_i) G(y_i) \right] e^{\int_{t_i}^{t_i} b(\gamma) G'(y) d\gamma} \\ & - n a_T'(T_i) F(x_i) e^{\int_{t_i}^{t_i} b(\gamma) G'(y) d\gamma} \\ & \int_{t_i}^{t_i} a(T) F'(x) e^{\int_{t_i}^{t_i} [b(\gamma) G'(y) - a(\gamma) F'(x)] d\gamma} d\beta \quad (29) \end{aligned}$$

The extremal condition on the yield of B at time θ demands the vanishing of $\frac{\partial y}{\partial T_i}$. Cancelling the common factor,

$$\int_{t_i}^{t_i} b(\gamma) G'(y) d\gamma$$

replacing t by θ , and suppressing the index i , there results

$$n a_T'(T) F(x) - b_T'(T) G(y) = n a_T'(T) F(x).$$

$$\int_{t_i}^{\theta} a(T) F'(x) e^{\int_{t_i}^{\theta} [b(\gamma) G'(y) - a(\gamma) F'(x)] d\gamma} d\beta \quad (30)$$

It should be remarked that T and x or y which enter as arguments of the functions under the integral signs, should be replaced by their expressions as functions of the respective summation variables β and γ . Using the definition of $A'(T)$, equation (13'),

$$\begin{aligned} 1 - \frac{1}{n} A(T) \frac{G(y)}{F(x)} = \\ \int_{t_i}^{\theta} a(T) F'(x) e^{\int_{t_i}^{\theta} [b(\gamma) G'(y) - a(\gamma) F'(x)] d\gamma} d\beta \quad (31) \end{aligned}$$

As before this integral expression may be transformed to a differential equation to give

$$\begin{aligned} \frac{1}{n} \frac{d}{dt} \left[A(T) \frac{G(y)}{F(x)} \right] = a(T) F'(x) \\ + \left[1 - \frac{1}{n} A(T) \frac{G(y)}{F(x)} \right] [b(t) G'(y) - a(T) F'(x)] \end{aligned}$$

which becomes

$$\frac{dT}{dt} = n B(T) \frac{F(x) G'(y)}{G(y)} \quad (32)$$

where $B(T)$ is defined in equation (18'). An immediate check is provided by a comparison of equations (15) and (32).

An elimination of x and y between $\frac{dT}{dt}$, $\frac{d^2 T}{dt^2}$, $\frac{d^3 T}{dt^3}$ would give the differential equation defining the shape of the temperature profile. Such an elimination may be carried out if $F(x)$ and $G(y)$ are given in explicit form, but the results are usually too complicated to justify the trouble.

6. EQUIVALENCE OF TWO PROBLEMS

In the introduction it was stated that another approach to the study of the optimum temperature profiles was possible; namely, to search for the minimum process time θ at which a given yield y_m of the product of interest can be attained. This problem is difficult to treat by the direct approach, but falls well within the possibilities of the implicit method. As an example of the application of this method, the problem for a system of two consecutive first order reactions will be solved. Consider again the system $A \rightarrow B \rightarrow C$ for which the kinetics are given by equations (8) and (9). The yield y of the component of interest B will be taken as the independent variable, and the reaction time t and concentration of feed component x as functions $t(y)$ and $x(y)$. This representation is proper and will not give rise to multivalued functions, provided values of y up to the maximum ($\frac{dy}{dt} = 0$) and not beyond it are taken.

Equations (8) and (9) may be written

$$\frac{dt}{dy} = \frac{1}{a(T)x - b(T)y} \quad (33)$$

$$\frac{dx}{dy} = \frac{-a(T)x}{a(T)x - b(T)y} \quad (34)$$

The process time θ is given by

$$\theta = \int_{y_0}^{y_m} \frac{dy}{a(T)x - b(T)y} \quad (35)$$

The limits y_0 and y_m are fixed, and T and x are to be replaced by their expressions as a function of y . It is desired to make the process time θ an extremum with respect to the variable T_i , which is now the temperature at $y = y_i$. The partial functional derivative of θ with respect to T_i is

$$\frac{\partial \theta}{\partial T_i} = - \int_{y_i}^{y_m} \frac{1}{(ax - by)^2} \left[a \frac{\partial x}{\partial T_i} + \delta(y - y_i) \cdot (a_T'x - b_T'y) \right] dy \quad (86)$$

To calculate the partial functional derivative of x with respect to T_i , apply the implicit method to equation (84)

$$\frac{d}{dy} \frac{\partial x}{\partial T_i} = \frac{aby}{(ax - by)^2} \frac{\partial x}{\partial T_i} + \delta(y - y_i) \frac{(ba_T' - ab_T')}{(ax - by)^2} xy$$

This gives

$$\begin{aligned} \frac{\partial x}{\partial T_i} &= \left[\frac{ba_T' - ab_T'}{(ax - by)^2} xy \right]_{y=y_i} e^{\int_{y_i}^y \frac{aby}{(ax - by)^2} dy}, \quad y \geq y_i \quad (87) \\ &= 0, \quad y < y_i \end{aligned}$$

The summation variables β and γ under the integral signs stand for the yield y . If equation (87) is substituted into equation (86) and the delta function term is integrated, one finds

$$\begin{aligned} \frac{\partial \theta}{\partial T_i} &= \frac{a_T'x - b_T'y}{(ax - by)^2} + \\ &\quad \frac{(ba_T' - ab_T')xy}{(ax - by)^2} \int_{y_i}^{y_m} \frac{a}{(ax - b\beta)^2} e^{\int_{y_i}^{\beta} \frac{aby}{(ax - by)^2} dy} d\beta \end{aligned}$$

The extremal condition on θ is therefore

$$\begin{aligned} \frac{a_T'x - b_T'y}{(ba_T' - ab_T')xy} + \\ \int_{y_i}^{y_m} \frac{a}{(ax - b\beta)^2} e^{\int_{y_i}^{\beta} \frac{aby}{(ax - by)^2} dy} d\beta = 0 \quad (88) \end{aligned}$$

On taking the corresponding differential equation

$$\begin{aligned} \frac{d}{dy} \left[\frac{x - Ay}{(b - aA)xy} \right] - \frac{a}{(ax - by)^2} + \\ \frac{x - Ay}{(b - aA)xy} \frac{ab}{(ax - by)^2} = 0 \end{aligned}$$

Since

$$dt = \frac{1}{ax - by} dy$$

there results

$$\frac{dT}{dt} = \frac{b - aA}{A_T'} \frac{x}{y}$$

which is the same expression as the one which was obtained for the temperature gradient for the problem of the maximum yield at constant process time. It may be remarked also from equation (88) that the zero functions are the same. Thus, at constant process time θ , there is a maximum yield $y = y_m$ of component B obtainable. If one seeks the shortest process time t in which to obtain a yield y_m , one finds that $t = \theta$. The two problems are therefore mathematically equivalent. This has been proved for this one case only, and to be rigorous should be proved for more general cases. However, from the calculus of variations it is known that if an extremum of a functional $I[T]$ under the condition of restraint

$$J[T] = \text{constant}$$

is sought, it is necessary to find the extremal functions which satisfy

$$\delta I + \mu \delta J = 0$$

according to the method of Lagrange multipliers. But this would also be the condition which would have to be satisfied if the extremum of $J[T]$ is required under the condition of restraint

$$I[T] = \text{constant}.$$

Therefore the result found might have been expected. More details about this may be found in COURANT and HILBERT [2].

7. DISCUSSION

In this paper methods of determining the optimum temperature gradient in a tubular reactor have been developed. The problem has been reduced to the solution of a system of ordinary differential equations which will be discussed in a succeeding paper. No rigorous justification of the procedures used has been given. While this seemed justified during the analysis in order to maintain its

practical value, some discussion of the points under question seems proper at this stage.

The first question which naturally arises is the validity of the solution. Will the temperature profile as calculated provide the maximum yield, or is there another arrangement of temperatures, for instance operation at the highest attainable temperature, which will give an even higher yield? The question also remains unanswered whether the problem has an optimum solution at all. This sort of question always arises when the calculus of variations is used. To be complete the proof should show that the extremum obtained is a maximum, and further that it is the maximum maximum in the sense that there is no other temperature distribution which will give a higher yield. The first part concerning the existence of the maximum can presumably be answered by examining the sign of the second variation while the second part requires variation in the large, rather than the small. These demonstrations are always very difficult, and it is customary in physical problems not to carry them through but to depend on intuition and numerical procedures to rule out the doubtful cases. This is unsatisfactory to many, but should be acceptable to most engineers and applied mathematicians.

NOTATION

A, B, C, D , etc. = chemical specie taking part in a reaction

$$A = \frac{b'_T(T)}{a'_T(T)}$$

$a(T), b(T), c(T)$, etc. = specific reaction velocity constants, generally of Arrhenius form

$$B = \frac{b(T) - a(T) A(T)}{A'_T(T)}$$

$$C = \frac{c'_T(T)}{a'_T(T)}$$

E = activation energy of a reaction

F = function defined by equation (2)

$F(x)$ = concentration effect in kinetic expression

$G(y)$ = concentration effect in kinetic expression

k = specific velocity constants

K = equilibrium constant for reaction

$M = x_0 + y_0 + z_0$, sum of initial concentrations

R = gas constant

r = activation energy ratio in a reaction

T = temperature in reactor

T_i = temperature at time t_i after entrance

t = time

t_i = particular instant of time

x, y, z = concentrations of A, B, C , respectively

$Z(t)$ = zero function—differently defined in each problem

θ = minimum time

Prime denotes differentiation with respect to subscript—generally T .

Subscript zero denotes initial condition.

Subscript 1, 2, 3, . . . denotes a particular reaction.

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The application of linear programming to design problems

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Abstract—It is the purpose of this paper to bring to the attention of the chemical engineering profession a recently developed mathematical technique, called "linear programming", which is exceedingly valuable in solving certain general problems connected with, *inter alia*, the efficient design of a chemical plant, and the discovery of an optimum production schedule which would maximize the profits of an enterprise. The general and more important features of linear programming will be discussed in the main body of this paper, while, in the Appendix, an illustrative problem of, it is hoped, general interest will be worked out numerically.

Résumé—Cet article a été écrit pour attirer l'attention des Ingénieurs du Génie Chimique sur une technique mathématique récemment développée et appelée "linear programming," extrêmement précieuse pour résoudre certains problèmes généraux relatifs, entre autres, à l'obtention d'un projet efficient d'une installation chimique et à la découverte d'un programme de production maximum qui porteraient à son maximum les profits d'une entreprise. Dans le corps de cet article, les auteurs traitent des caractéristiques générales les plus importantes du "linear programming," tandis qu'en appendice ils étudient numériquement un exemple d'intérêt général.

A SIMPLE PROBLEM

It is believed that an easy introduction into the main ideas of linear programming can be made by considering the following simple problem.

A certain entrepreneur has at his disposal two raw materials, *A* and *B*, fixed price, which can be reached in different ways to produce two products, *C* and *D*, which he can sell, again, at a fixed price. We shall assume, moreover, that the two processes, which the entrepreneur may employ, are fixed in the sense that both the amounts of *A* and *B* consumed in, and the cost of operating, each process per pound of product, are predetermined parameters which cannot be altered. The following question then arises: If we suppose that the available supply, per unit of time, of *A* and *B* cannot exceed, for one reason or another, certain upper limits, then at what rates must the entrepreneur produce the two products, *C* and *D*, in order to maximize his profits?

The above problem will now be solved by an elementary method. Let first

x_i = rate (or level) at which process *i* is operated ($i = 1, 2$).

a_{ji} = amount of raw material *j* consumed in process *i*, when the process *i* is operated at a unit rate ($j, i = 1, 2$).

c_i = net profit from selling the product of process *i*, when this process is operated at a unit rate.

s_i = maximum available rate of supply of the raw material *i*.

r = the total profit per unit time.

In mathematical language then, it can be said that the entrepreneur desires to maximize the linear function

$$r = c_1 x_1 + c_2 x_2 \quad (1)$$

where the only two variables at his disposal, x_1 and x_2 , are subject to the conditions

$$a_{11} x_1 + a_{12} x_2 \leq s_1 \quad (2a)$$

$$a_{21} x_1 + a_{22} x_2 \leq s_2 \quad (2b)$$

and where the parameters a_{ji} , s_i and c_i are fixed.

Moreover, we must obviously require that,

$$x_1 \geq 0 \text{ and } x_2 \geq 0 \quad (2c)$$

Now, let us consider the quadrangle $OGHK$, shown in Fig. 1. It is at once clear that any point (x_1, x_2) which satisfies equations (2a), (2b) and (2c) must not lie outside $OGHK$, and moreover that the line

$$x_1 = -\frac{c_2}{c_1}x_2 + \frac{r}{c_1} \quad (3)$$

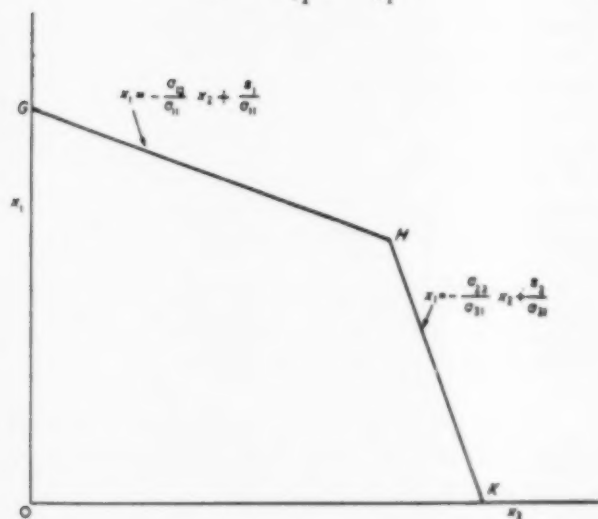


FIG. 1

must pass through $OGHK$, or one of its four corners. Finally, since r is the only unknown parameter in equation (3), the maximum value of r is proportional to the greatest permissible intercept of equation (3) with the x_1 -axis. It is not difficult therefore to show that three cases arise.

1. If $\frac{c_2}{c_1} > \frac{a_{22}}{a_{21}}$, then the point (x_1, x_2) which maximizes r , is K .

2. If $\frac{a_{12}}{a_{11}} < \frac{c_2}{c_1} < \frac{a_{22}}{a_{21}}$, then the optimum production schedule is given by H .

3. If $\frac{c_2}{c_1} < \frac{a_{12}}{a_{11}}$, then G is the optimum point.

As a simple numerical example consider the following: The two reactions are

1. 1 pound of A + 1 pound of $B \rightarrow 2$ pounds of C
2. 1 pound of A + 2 pounds of $B \rightarrow 3$ pounds of D

and

$$s_1 = 100 \text{ pounds of } A/\text{day}$$

$$s_2 = 150 \text{ pounds of } B/\text{day}$$

$$c_1 = 1 \text{ dollar per pound of } C$$

$$c_2 = 0.80 \text{ dollars per pound of } D$$

Therefore equations (2a) and (2b) become

$$\frac{1}{2}x_1 + \frac{1}{3}x_2 < 100$$

$$\frac{1}{2}x_1 + \frac{2}{3}x_2 < 150$$

Now, since $\frac{2}{3} < \frac{c_2}{c_1} < \frac{4}{3}$, the point H , in Fig. 1,

represents the optimum production schedule, and

$$x_1 = 100 \text{ pounds per day}$$

$$x_2 = 150 \text{ pounds per day}$$

On the other hand, if

$$c_2 = 0.60 \text{ dollars per pound of } D,$$

then the optimum production schedule would be

$$x_1 = 200 \text{ pounds per day}$$

$$x_2 = 0$$

We perceive therefore that, in this simple case in any event, the production schedule, which maximizes the total revenue r , depends in a discontinuous manner on the various fixed parameters of the problem, namely the coefficients a_{ij} , c_i and s_i , and that, moreover, this optimum point (x_1, x_2) is situated at one of the corners of the convex polygon $OGHK$. Finally, it can be said that, due to the peculiar nature of the restrictions which the two variables x_1 and x_2 must satisfy, this problem just illustrated could not have been solved by the methods of differential calculus.

THE MATHEMATICAL FORMULATION OF THE GENERAL PROBLEM

So far, only a very simple special case has been considered. However, the problem can easily be generalized as follows. It is supposed now that

the entrepreneur has at his disposal n raw materials, in limited supply, which he can use in k predefined processes to produce certain goods. And again he desires to determine the optimum production schedule which would maximize his profits. Stated mathematically, one is asked to calculate the values of x_1, x_2, \dots, x_k (that is, the rates at which the various processes should be operated) which would maximize the linear expression

$$r = c_1 x_1 + c_2 x_2 + \dots + c_k x_k \quad (4)$$

with the restrictions

$$a_{j1} x_1 + a_{j2} x_2 + \dots + a_{jk} x_k \leq s_j \text{ for } j = 1, 2, \dots, n \quad (5a)$$

and

$$x_i \geq 0 \text{ for } i = 1, 2, \dots, k \quad (5b)$$

Of course, the parameters c_i , a_{ji} and s_j are assumed to have been specified *a priori*.

Now, it was shown earlier how a simplified version of the above problem could be solved by a graphical method. More complicated cases can be handled by a recently discovered technique called linear programming. Strictly speaking, linear programming has been defined as the study of the maximization or minimization of a linear expression, where the variables in that expression are restricted by a set of linear inequalities. Such a system is described by equations (4), (5a) and (5b); it can be solved by a number of methods, the most common of which is the "Simplex Method." In essence, this "Simplex Method" is an iterative procedure; that is, one starts with a set of values for x_1, x_2, \dots, x_k which satisfy equations (5a) and (5b), and then calculates another set of values for the above mentioned variables, which increases the total revenue. This procedure is then repeated until r is maximized. In addition, the method is simple enough, to be adaptable to machine calculations.

Problems in maximization, or minimization, which can be treated by the methods of linear programming, are encountered very frequently in connection with, to mention only a few cases, the efficient design of a chemical plant, and a large variety of planning operations. To be sure,

there are severe limitations on the method. For one thing, the assumption that the purchasing price of the raw materials and the selling price of the products are known in advance and are independent of the rate of consumption or the rate of production of the substances is, usually, an over simplification of the real situation. Also, the "Simplex Method," in its present form, holds only when the number of processes available to the entrepreneur, is finite. In spite of these restrictions, however, there are large numbers of important practical problems, to which the system of equations (4), (5a) and (5b) would apply with sufficient accuracy, and which therefore could be investigated by the methods of linear programming. For a much more detailed account of the subject, as well as extensive references, one could consult the books by DORFMAN [1] and by CHARNES, COOPER and HENDERSON [2].

APPENDIX

AN ILLUSTRATIVE EXAMPLE

The numerical example to be presented now will be worked out by the so-called "Simplex Method," which is the most commonly used procedure for solving problems of the linear programming type. The notation of Reference [2] will be used throughout this appendix. This reference should also be consulted for the details of the "Simplex

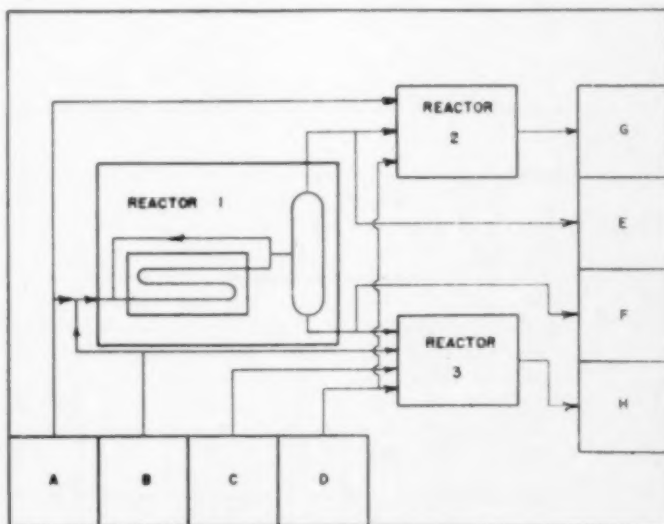


FIG. 2. Flow diagram for the illustrative problem.

Method," as well as for instructions concerning the use and construction of the "Simplex Tableau." The purpose of this example is merely to illustrate the types of problems that can be analysed by this method, and to give some idea about the amount of work needed to perform the calculations.

The flowsheet of a hypothetical chemical plant is shown in Fig. 2. The plant produces four products, *G*, *E*, *F* and *H*, and consumes four raw materials *A*, *B*, *C* and *D* in limited supply. The four available processes are depicted schematically in Figs. 3 to 6.

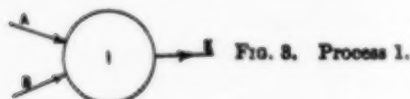


FIG. 3. Process 1.

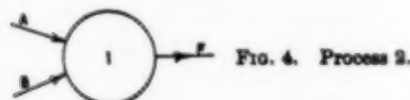
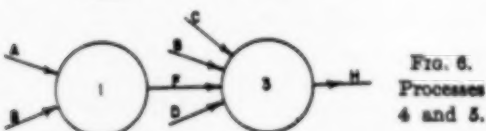


FIG. 4. Process 2.

FIG. 5.
Process 3.FIG. 6.
Processes
4 and 5.

Schematic diagrams of Processes 1, 2, 3, 4 and 5 of the illustrative problem. Processes 4 and 5 are identical in all respects except for the net profit.

The following data are given:

Raw material	Maximum available supply	Cost
<i>A</i>	400 lb./day	\$1.50/lb.
<i>B</i>	300 lb./day	\$2.00/lb.
<i>C</i>	100 lb./day	\$4.50/lb.
<i>D</i>	250 lb./day	\$2.50/lb.

Process	Pounds of raw material consumed				Cost of reaction	Selling price of product
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>		
1	2	1	0	0	\$1.50/lb. <i>A</i>	\$3.00 /lb.
2	2	1	0	0	\$0.50/lb. <i>A</i>	\$2.38 1/2 /lb.
3	3	1	0	2	\$1.00/lb. <i>G</i>	\$3.75 /lb.
4	2	7	3	3	\$2.00/lb. <i>H</i>	\$5.00 /lb.

It is also stated that the reaction cost of Process 4 is \$2.00/lb. *H* only up to 75 lbs. of *H* per day, and that for any additional *H* produced, the reaction cost is \$2.20 per pound of *H*. So, in essence, the number of processes is equal to five.

Following a well established procedure [1], we shall introduce five disposal processes, numbers 6, 7, 8, 9 and 10, which dispose of, respectively, raw materials *A*, *B*, *C*, *C'* and *D*. *C'* is that part of the substance *C* which is used exclusively in process 4, while *C''* is used exclusively in process 5.

If now, x_i , $1 \leq i \leq 5$, denotes the net profit from process *i*, in dollars per day, and x_i , $6 \leq i \leq 10$, measures the rate of disposal by process *i* in pounds per day, the following five equations are obtained:

$$2x_1 + 2x_2 + \frac{3}{2}x_3 + \frac{1}{2}x_4 + \frac{2}{3}x_5 + 1x_6 + 0x_7 + 0x_8 + 0x_9 + 0x_{10} = 400$$

$$1x_1 + 1x_2 + \frac{1}{2}x_3 + \frac{7}{6}x_4 + \frac{7}{6}x_5 + 0x_6 + 1x_7 + 0x_8 + 0x_9 + 0x_{10} = 300$$

$$0x_1 + 0x_2 + 0x_3 + \frac{1}{2}x_4 + 0x_5 + 0x_6 + 0x_7 + 1x_8 + 0x_9 + 0x_{10} = 15$$

Table 1. Simplex Tableau, First Stage.

<i>i</i>	<i>C_i</i>	<i>P₀</i>	<i>P₁</i>	<i>P₂</i>	<i>P₃</i>	<i>P₄</i>	<i>P₅</i>	<i>P₆</i>	<i>P₇</i>	<i>P₈</i>	<i>P₉</i>	<i>P₁₀</i>
1	1	200	1	1	3/4	1/6	1/3	1/2	0	0	0	0
7	0	100	0	0	-1/4	1	2	-1/2	1	0	0	0
8	0	15	0	0	0	1/2	0	0	0	1	0	0
9	0	85	0	0	0	0	1	0	0	0	1	0
10	0	250	0	0	1	1/2	1	0	0	0	0	1
Profit		200	0	0	1/4	5/6	2/3	-1/2	0	0	0	0

Now use x_4 as the new active process. $\min_j \frac{x_{10}}{x_{j4}} = 30$ at $j = 8 = 4$. $x'_{4j} = \frac{x_{10}}{x_{44}} = \frac{x_{10}}{1/2} = 2x_{4j}$; $x'_{ij} = x_{ij} - 2x_{4j}x_{44}$.

Table 2. Simplex Tableau, Second Stage.

i	C_i	P_0	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
1	1	195	1	1	3/4	0	1/3	-1/2	0	-1/3	0	0
7	0	70	0	0	-1/4	0	2	-1/2	1	-2	0	0
4	1	30	0	0	0	1	0	0	0	2	0	0
9	0	85	0	0	0	0	1	0	0	0	1	0
10	0	235	0	0	1	0	1	0	0	-1	0	1
Profit		225	0	0	1/4	0	2/3	-1/2	0	-5/3	0	0

Now use x_8 as the new active process. $\min_j \frac{x_{10}}{x_{78}} = 35$ at $j = 7 = r$; $x'_{8j} = \frac{x_{7j}}{x_{78}} = \frac{1}{2} x_{7j}$ and $x'_{ij} = x_{ij} - \frac{1}{2} x_{7j} x_{15}$.

Table 3. Simplex Tableau, Third Stage.

i	C_i	P_0	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
1	1	188 1/2	1	1	19/24	0	0	7/12	-1/6	0	0	0
5	1	35	0	0	-1/8	0	1	-1/4	1/2	-1	0	0
4	1	30	0	0	0	1	0	0	0	2	0	0
9	0	50	0	0	1/8	0	0	1/4	-1/2	1	1	0
10	0	200	0	0	9/8	0	0	1/4	-1/2	0	0	1
Profit		248 1/2	0	0	1/3	0	0	-1/3	-1/3	-1	0	0

$$\min_j \frac{x_{10}}{x_{98}} = \frac{1000}{9} = 177.77 \dots r = 10; x'_{8j} = \frac{x_{10j}}{x_{108}} = \frac{8}{9} x_{10j}; x'_{ij} = x_{ij} - \frac{8}{9} x_{10j} x_{15}.$$

$$0x_1 + 0x_2 + 0x_3 + 0x_4 + 1x_5 + 0x_6 + 0x_7 + 0x_8 + 1x_9 + 0x_{10} = 85$$

$$0x_1 + 0x_2 + 1x_3 + \frac{1}{2}x_4 + 1x_5 + 0x_6 + 0x_7 + 0x_8 + 0x_9 + 1x_{10} = 250$$

The first "Simplex Tableau" is obtained by letting $x_3 = x_8 = x_4 = x_5 = x_6 = 0$, and the procedure thereafter is identical with that employed by [2]. It will be seen that the problem will be solved by just three iterations.

We see then that the "Simplex Criterion" [1] is now satisfied, and that therefore $r = 307 \frac{16}{27}$ dollars per day is the maximum attainable profit under the conditions of the problem. Four active processes are used, namely pro-

cesses 1, 3, 4 and 5, together with one disposal process, No. 9. It can also be observed that since processes 1 and 2 give the same profit, the levels at which they operate could be interchanged without varying the total net revenue.

Acknowledgement—It is a pleasure for the authors to acknowledge the help of Dr. THOMAS BARON, who introduced them to the subject of linear programming, and at whose suggestion this article was written. The comments of Dr. E. E. PETERSEN are also appreciated.

Table 4. Simplex Tableau, Fourth Stage.

i	C_i	P_0	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
1	1	$42\frac{16}{27}$	1	1	0	0	0	$11/27$	$5/27$	0	0	$-\frac{19}{27}$
5	1	$57\frac{2}{9}$	0	0	0	0	1	$-2/9$	$4/9$	-1	0	$1/9$
4	1	30	0	0	0	1	0	0	0	2	0	0
9	0	$27\frac{7}{9}$	0	0	0	0	0	$2/9$	$-4/9$	1	1	$-1/9$
3	1	$177\frac{7}{9}$	0	0	1	0	0	$2/9$	$-4/9$	0	0	$8/9$
Profit		$307\frac{16}{27}$	0	0	0	0	0	$-\frac{11}{27}$	$-\frac{5}{27}$	-1	0	$-\frac{8}{27}$

REFERENCES

- [1] DORFMAN, R.; *Application of Linear Programming to the Theory of the Firm*. University of California Press.
 [2] CHARNES, A., COOPER, W. W. and HENDERSON, A.; *An Introduction to Linear Programming*. John Wiley & Sons.

Book reviews

O. A. HOUGEN, K. M. WATSON, R. A. RAGATZ : **Chemical Process Principles, Part I**, 2nd edition. 504 pp. 129 figures. Chapman & Hall. 68s.

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This is a second edition of an important book that can be warmly recommended to all chemical engineers. It is one of the few books to treat specifically the subject of material and energy balances. The subject is one with which all chemical engineers should be intimately familiar, both because of its utility in drawing up quantitative flow sheets for plant design, and its value in interpreting experimental results from existing plant. These two applications are amply recognized by the authors who give large numbers of worked examples and problems from industrial practice. The book is primarily a University teaching text, but sufficient modern data on vapour pressures, heat capacities, heats of formation, combustion and dilution are given to make it valuable as a reference work for the design or plant engineer.

The second edition has two more chapters than the first, one dealing with mathematical procedures and the other with adsorption. The rest of the book has been carefully revised, new problems have been added, and numerical answers are now given to about half the problems, and ought to have been given for the lot; numerical problems without answers are almost useless to the student working by himself. The printing and layout have been much improved; unfortunately the price has increased.

The book could usefully be shortened by deleting the

first three chapters. These deal respectively with mathematical procedures, stoichiometric relationships, and the behaviour of ideal gases. The student who has not grasped this elementary mathematics, chemistry and physics will not read a book on chemical process principles, nor will he learn it from so few pages. Specialized matters such as the properties of triangular diagrams, excellently explained in Chapter 1, could be moved to the part dealing with ternary systems, rather than treated in the abstract.

Another addition which has a doubtful place in this book is a somewhat detailed study of stagewise solvent extraction processes in Chapter 6. This would seem to be trespassing on another field, and further excursions of this kind would lead to a book on Unit Operations under the title "Material and Energy Balances."

The new Chapter 10 on adsorption is a valuable expansion of the short section in the first edition. There are also numerous revisions which must have cost much labour; the thermochemical data is based on 25°C instead of 18°C. Modern data on critical properties is given. New examples of current industrial interest are a two page discussion of nuclear reactors, a worked example dealing with a fluid catalytic cracker, and a discussion of time lag in stirred vessels has been included.

It is gratifying that the authors have not allowed this useful book to get out of date. We await the second edition of Volumes II and III with great interest.

J. F. DAVIDSON

S. W. FERRIS : **Handbook of Hydrocarbons**, Academic Books Ltd., London, 1955. 324 pages. 68s.

THE writer of the book, who is affiliated with the Research Development Department of the Sun Oil Company, Marcus Hook, Pa., U.S.A., has written a valuable contribution. The book is indeed a help to those investigators who are connected with hydrocarbon research.

In Table A the hydrocarbons are listed in the order of the boiling points at 760 mm of mercury; n (refractive index), d (specific gravity), and melting point are included.

In Table B the listing is done in the order of the empirical formula. The hydrocarbons of the same type are brought in separate groups.

Both tables take up a total of 200 pages. The remaining 34 pages are used for Table C which gives alternate names

for hydrocarbons (19 pages), and for Table D (9 pages) in which a survey is given of representative cyclic hydrocarbons.

In an appendix correction, figures for boiling points are given and nomographs for correcting observed boiling points at a certain pressure to e.g. 760 mm of mercury.

The writer of this review expresses his gratitude for the enormous amount of work which Mr. S. W. FERRIS must have undertaken to compile the data in question. The book will prove to very be useful. Analogous works are desirable in which other physical constants, e.g. viscosity and surface tension, can be considered, if possible at different temperatures. Perhaps the author can later find time to handle these constants also.

H. I. WATERMAN

Algal Culture from Laboratory to Pilot Plant. Edited by JOHN S. BURLEW. Carnegie Institution of Washington Publication 600. Washington, D.C. 1953. ix + 357 pp. 92 figs. Price \$1.25.

THE large scale production of green algae by continuous culture under controlled conditions means in effect the translation of farming into chemical engineering terms. It is natural, therefore, that the project should be greeted with enthusiasm by chemical engineers, and with reserve by those whose business it is to improve the methods of conventional agriculture. This report is invaluable as a summary of the investigations which have been carried out since the end of the war, but it leaves unsettled the questions of whether, and in what circumstances, the process may ever prove to be economic or quasi-economic.

Most of the experimental work has been carried out with algae belonging to a few species of the genus *Chlorella*, largely because this is a familiar laboratory organism whose habits are fairly well known; it seems also to be reasonably suitable for large-scale culture, although it is possible that some other of the many types of algae might prove to be superior. *Chlorella* is a microscopic green plant which grows in suspension in water, reproducing itself by simple division. It is autotrophic – that is, it requires no nutrients of organic origin; it uses visible light to synthesize its substance from carbon dioxide and inorganic nitrogen compounds (such as nitrates or ammonia), together with phosphate, potassium and a number of other necessary inorganic nutrients, including the imperfectly characterized micro-nutrients or trace elements. The dried cells contain some 50% protein and 10% fat, the remainder being mostly carbohydrate. The protein contains all the ten amino-acids known to be essential in the human diet although, like all vegetable protein, it contains too little methionine. Feeding tests on rats and chicks have shown it to be comparable to yeast, but inferior to skimmed milk.

Primarily, *chlorella* is to be regarded as a potential provider of protein, which is in chronically short supply in the world. The enthusiasts suggest that at any rate in some parts of the world, where agricultural land is scarce or over-populated – for instance, India, Japan or Israel – the scientific cultivation of *Chlorella* would be justified by the high yield of protein per unit area of ground which is made possible by continuous as against seasonal growth. Under such circumstances the process would not necessarily have to be economically competitive with conventional agriculture, as it would, for instance, in order to be worth while in the U.S.A. The sceptic might reply that only a virtually starving population would eat *Chlorella*, and that the money and effort might more profitably be devoted to improvements in agricultural practice, for which there is still great scope in most countries.

A plant for the large-scale culture of algae would be, in

effect, a continuous stirred tank reactor of the type so familiar to chemical engineers. The nutrient medium is fed continually to the culture, which is drawn off at the same rate. The culture itself must be agitated to maintain uniformity of composition and to keep the cells in suspension. The composition and feed-rate of the solution should be such as to maintain the optimum nutrient composition and cell concentration in the culture, which should be kept saturated with CO_2 at an appropriate partial pressure (about 0.05 atm) and maintained at a suitable temperature (heating or cooling may be required, depending on the climate). It seems probable that satisfactory results can only be obtained by enclosing the culture under a transparent cover to keep in CO_2 , prevent evaporation (in regions where water is scarce) and exclude contaminating organisms. A pilot plant constructed on these lines was constructed and operated from July to December 1951, in Massachusetts. The culture was circulated through a wide polythene tube, which flattened out to a width of about 4 ft. and contained an inch or so of liquid and a gas space which was filled with 5% CO_2 in air. Nearly 100 lb. (dry weight) of *Chlorella* was grown and harvested, and the results suggested that a yield of some 17½ tons per acre (7.3 kg./m²) per year might be obtained from a plant of this type. This represents a yield of protein much higher than can be obtained from conventional crops, but it is clear that the capital charges and running costs (much of the latter for power consumed in pumping) would be of a different order from those for an equal area of agricultural land.

There is no space here to discuss the many technical problems arising in the design and operation of a continuous culture plant. These include the economic harvesting and drying of the algae; the question of whether the medium can be recycled with no treatment but the addition of fresh nutrients; the danger of contamination by protozoa; the supply of trace elements and the use of chelating agents to buffer their concentration; the waste of light by unproductive absorption in the upper layers, and the possibility of mitigating it by making use of the "intermittent illumination" effect; and many others. The report contains many studies of such problems by various contributors in the U.S.A., England, Japan, Israel and Germany.

It is difficult to come to any confident conclusion about the future of the large scale cultivation of algae. However, two points are suggested by a study of this report. Firstly, in any project of this kind, competent chemical engineers should be brought in at an early stage if the matter is not to remain indefinitely at the level of a laboratory investigation; and secondly, the dangerous fascination of the technical problems involved may lead to the diversion of much valuable scientific and technical talent from work of more immediate promise.

P. V. DANCKWERTS.